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# DESCRIPTION

## Field of the Invention

**[0001]** The present invention relates to methods of re-dispersing and de-agglomerating dewatered, partially dried and dried compositions of microfibrillated cellulose into liquid compositions comprising same, by applying ultrasonic energy to such liquid compositions of dewatered, partially dried and dried compositions of microfibrillated cellulose, or compositions of microfibrillated cellulose and inorganic particulate material.

## Background of the Invention

**[0002]** Microfibrillated cellulose and, optionally, inorganic particulate materials, for example an alkaline earth metal carbonate (e.g., calcium carbonate) or kaolin, are used widely in a number of applications. These include the production of microfibrillated cellulose and, optionally, mineral containing compositions, which may be used as fillers in paper manufacture and/or in paper coatings. In paper and coated paper products, such fillers are typically added to replace a portion of other more expensive components of the paper and/or coated paper product. Fillers may also be added with an aim of modifying the physical, mechanical, and/or optical requirements of paper and/or coated paper products. Clearly, the greater the amount of filler that is included, the greater potential for cost savings. However, the amount of filler added and the associated cost saving must be balanced against the physical, mechanical and optical requirements of the final paper product or coated paper product. Thus, there is a continuing need for the development of improved fillers for paper and paper coatings, which for use at a high loading level without adversely affecting the physical, mechanical and/or optical requirements of such paper and/or coated paper products. There is also a need for the development of methods for preparing such fillers economically.

**[0003]** The present invention seeks to provide alternative and/or improved fillers for paper and/or coated paper products which may be incorporated in the paper and/or coated paper product at relatively high loading levels, whilst maintaining or even improving the physical, mechanical and/or optical properties of the paper and/or coated paper product. The present invention also seeks to provide an economical method for preparing such fillers. As such, the present inventors have surprisingly found that a filler comprising microfibrillated cellulose and, optionally, an inorganic particulate material, is prepared by economical methods and is loaded in paper products and/or coated paper products at relatively high levels, whilst maintaining or even improving the physical, mechanical and/or optical properties of the final paper product. The application of ultrasonic energy to a suspension of microfibrillated cellulose, or microfibrillated cellulose suspensions comprising at least one inorganic particulate material has surprisingly been found to efficiently produce such suspensions having improved tensile strength and/or enhanced viscosity properties.

**[0004]** Further, the present invention seeks to address the problem of preparing microfibrillated cellulose and microfibrillated cellulose and inorganic particulate material compositions economically on an industrial scale. Current methods of microfibrillating cellulosic material and microfibrillated cellulose and inorganic particulate material require relatively high amounts of energy, owing in part to the relatively high viscosity of the starting material and the microfibrillated-containing product, and a commercially viable process for preparing microfibrillated cellulose on an industrial scale has hitherto before proved elusive.

**[0005]** Additionally, the present invention seeks to address the problem of re-dispersing dewatered, partially dried or essentially dried microfibrillated cellulose compositions or microfibrillated cellulose and inorganic particulate matter compositions in a liquid medium, optionally in the presence of an additive other than inorganic particulate material and/or in the presence of a combination of inorganic particulate materials. The additive and/or combination of inorganic particulate materials may, for example, enhance a mechanical and/or physical property of the re-dispersed microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material composition. The present invention further relates to compositions comprising re-dispersed microfibrillated cellulose and, optionally, inorganic particulate material and the use of re-dispersed microfibrillated cellulose and, optionally, inorganic particulate material, in an article, product or composition. The solution to the problem is to apply ultrasonic energy in the re-dispersion of compositions of microfibrillated cellulose or compositions of microfibrillated cellulose and at least one inorganic particulate material as herein described.

### **Summary of the Invention**

**[0006]** The present invention is based on the claims.

**[0007]** According to a first aspect, the present invention is directed to a method for re-dispersing dewatered, partially dried or essentially dried microfibrillated cellulose, the method comprising the steps of:

1. (a) adding a quantity of a suitable dispersing liquid (e.g., water) to a tank having at least one inlet and an outlet, wherein the tank further comprises a mixer and a pump attached to the outlet;
2. (b) adding a quantity of dewatered, partially dried or essentially dried microfibrillated cellulose to the tank through the at least one inlet in sufficient quantity to yield a liquid composition of microfibrillated cellulose at a desired solids concentration of 0.5 to 5% fibre solids;
3. (c) mixing the dispersing liquid and the dewatered, partially dried or essentially dried microfibrillated cellulose in the tank with the mixer to partially de-agglomerate and re-disperse the microfibrillated cellulose to form a flowable slurry;
4. (d) pumping the flowable slurry with the pump to an inlet of a flow cell, wherein the flow cell comprises one or more sonication probe in series and at least one outlet, wherein

the second outlet of the flow cell is connected to the second inlet of the tank, thereby providing for a continuous recirculation loop providing for the continuous application of ultrasonic energy to the slurry for a desired time period and/or total energy input range, wherein the flow cell comprises an adjustable valve at the second outlet to create back pressure of the recirculated slurry of from 0 to 4 bar, further wherein the liquid composition comprising microfibrillated cellulose of step (c) is continuously recirculated through the recirculation loop at a temperature of 20°C to 50°C;

5. (e) applying ultrasonic energy input to the slurry of 200 to 10,000 kWh/t continuously by the sonication probe at a frequency range of 19 to 100 kHz and at an amplitude of up to 60%, up to 100% or up to 200% to the physical limitations of the sonicator used for 1 to 120 minutes;
6. (f) collecting the re-dispersed suspension comprising microfibrillated cellulose with enhanced tensile strength and/or viscosity properties from the first outlet of the flow cell in a suitable holding vessel.

**[0008]** Prior art document JPS58206601A also relates to a method for re-dispersing dewatered, partially dried or essentially dried microfibrillated cellulose. However, according to this publication, water is added to the dried microfibrillated cellulose, rather than that the dried microfibrillated cellulose is added to the water. The document mentions the use of ultrasonication for dispersion of the microfibrillated cellulose with an ultrasonic frequency of at least 10 kHz. No mention is made of the total input of ultrasonic energy. The temperature of the dispersion during sonication was not specified. The use of a flow cell in a recirculation loop for the sonication process was not disclosed.

**[0009]** A further prior art document US2015/0225550 relates to a method for re-dispersing dewatered, partially dried or essentially dried microfibrillated cellulose using ultrasonic disperser. The use of a flow cell in a recirculation loop for the sonication process was not disclosed. Details of the ultrasonication process, such as operating pressure, temperature, frequency and energy input were not mentioned nor suggested in the document.

**[0010]** Another prior art document US2010/0279019 relates to ultrasonic treatment of suspended nanocrystalline cellulose (NCC) material not of a dispersion of microfibrillated cellulose. The sonication process of this document is carried out with an energy input of 50 to 25,000 joules/g; The use of a flow cell in a recirculation loop for the sonication process was not disclosed. Further details of the ultrasonication process are described in specific examples (e.g. sonication by means of a sonicator probe at 50-80% amplitude or 8-10 Watts in 4 second pulses with 4 seconds intervals to a total energy input of 3700 J/g of cellulose material.

**[0011]** Hence neither of the above prior art documents discloses nor suggest the present invention.

**[0012]** According to a second aspect, the present invention is directed to process of the first

aspect, wherein the dewatered, partially dried or essentially dried microfibrillated cellulose composition further comprises at least one inorganic particulate material.

**[0013]** In an embodiment of the first or second aspect of the present invention the cumulative ultrasonic energy input is from about 1,000 kWh/t to about 10,000 kWh/t or between about 1,000 kWh/t and about 2,000 kWh/t, or about 2,000 kWh/t to about 3,000 kWh/t.

**[0014]** In an embodiment of the first or second aspect of the present invention the flow cell comprises a cooling jacket for maintaining a temperature of the suspension of microfibrillated cellulose in the range of about about 20° C to about 50° C., or at room temperature, or about 20° C.

**[0015]** In an embodiment of the first or second aspect of the present invention the flow cell comprises an adjustable valve at the second outlet to create back pressure of the recirculated liquid of from about 3 bar.

**[0016]** In an embodiment of the first or second aspect of the present invention, the flow cell further comprises one or more boosters to mechanically increase or decrease the amplitude of the at least one sonication probe.

**[0017]** In the present invention, the ultrasonic energy is applied for about 1 to about 120 minutes, or about 1 to about 90 minutes, or about 1 to about 75 minutes, or about 1 to about 60 minutes, or about 1 to about 45 minutes or about 1 to about 30 minutes.

**[0018]** In an embodiment of the first aspect of the present invention, the microfibrillated cellulose is pelletized, and in the second aspect, microfibrillated cellulose and inorganic particulate material is pelletized.

**[0019]** In an embodiment of the first and second aspects of the present invention, the ultrasonic energy is applied until a specified cumulative energy input is achieved. In additional embodiments, the cumulative energy input is greater than 200 kWh/t, greater than 400 kWh/t, or greater than 500 kWh/t, or greater than 1,000 kWh/t, or greater than 1,500 kWh/t, or greater than 2,000 kWh/t, or greater than 2,500 kWh/t, or greater than 3,000 kWh/t, or greater than 4,000 kWh/t, or greater than 5,000 kWh/t, or greater than 6,000 kWh/t, or greater than 7,000 kWh/t, or between 200 kWh/t and 10,000 kWh/t., or about 200 kWh/t and 5,000 kWh/t, or about 200 kWh/t and 4,000 kWh/t, or about 200 kWh/t and 3,000 kWh/t, or about 200 kWh/t and 2,000 kWh/t.

**[0020]** In an embodiment of the second aspect of the present invention, the recirculation loop comprises a high shear mixer.

**[0021]** In an embodiment of the first and second aspects of the present invention, the FLT index for the suspension of microfibrillated cellulose and the suspension of the microfibrillated cellulose and inorganic particulate material reaches 7.5 Nm/g or more, 7.5 Nm/g or more, 8

Nm/g or more, 8.5 Nm/g or more, 9 Nm/g or more, 9.5 Nm/g or more, 10 Nm/g or more, 10.5 Nm/g or more, 11 Nm/g or more, 11.5 Nm/g or more, 12 Nm/g or more, 12.5 Nm/g or more, 13 Nm/g or more, 13.5 Nm/g or more, 14 Nm/g or more, 14.5 Nm/g or more, or 15 Nm/g or more, through the methods disclosed in the specification.

**[0022]** In an embodiment of the first and second aspects of the present invention, the FLT index may be improved by about 5%, about 6%, about 7%, about 7.5%, about 8%, about 9%, about 10%, about 12.5%, about 15% or about 20%, or more, compared to suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material produced without the application of ultrasonic energy treatment to the slurry or suspension.

**[0023]** In an embodiment of the first and second aspects of the present invention, viscosity is improved by about 5%, about 6%, about 7%, about 7.5%, about 8%, about 9%, about 10%, about 12.5%, about 15% or about 20%, or more, compared to suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material produced without the application of ultrasonic energy treatment to the slurry or suspension.

**[0024]** In embodiments of the first and second aspects of the present invention, the microfibrillated cellulose is prepared from a chemical pulp, or a chemithermomechanical pulp, or a mechanical pulp, or a recycled pulp, or a paper broke pulp, or a papermill waste stream, or waste from a papermill, or combinations thereof.

**[0025]** In embodiments of the second aspect of the present invention, the inorganic particulate material comprises alkaline earth metal carbonate or sulphate, such as calcium carbonate, magnesium carbonate, dolomite, gypsum, a hydrous kandite clay such as kaolin, halloysite or ball clay, an anhydrous (calcined) kandite clay such as metakaolin or fully calcined kaolin, talc, mica, perlite or diatomaceous earth, or combinations thereof. In certain embodiments, calcium carbonate and/or kaolin are particularly preferred.

**[0026]** In embodiments of the first aspect of the present invention, the suspensions of microfibrillated cellulose, or with enhanced viscosity and tensile strength properties obtained by the method are suitable for use in a method of making paper or coating paper, paints and coatings, inks, oilfield chemicals, composites, consumer products, cosmetic products, pharmacological products and food product.

**[0027]** In embodiments of the second aspect of the present invention the suspensions of microfibrillated cellulose and inorganic particulate material with enhanced viscosity and tensile strength properties obtained by the method are suitable for use in a method of making paper or coating paper, paints and coatings, inks, oilfield chemicals, composites, consumer products, cosmetic products, pharmacological products and food product.

#### **Brief Description of the Drawings**

**[0028]**

Figure 1 is a SEM micrograph of microfibrillated cellulose prepared with ground calcium carbonate (GCC).

Figure 2 shows the effect of exposure to an ultrasonic bath on microfibrillated cellulose (MFC) viscosity.

Figure 3 shows the effect of exposure to an ultrasonic probe on FLT index (Nm/g).

Figure 4 shows the effect of exposure to an ultrasonic probe on microfibrillated cellulose (MFC) viscosity.

Figure 5 shows the effect of exposure to pulsed ultrasound on microfibrillated cellulose (MFC).

Figure 6 shows the effect of ceramic media contamination on microfibrillated cellulose (MFC) exposed to ultrasonication.

Figure 7 shows the effect of ultrasonication on a 50% percentage of pulp (POP) pressed cake.

Figure 8 shows the effect of high shear and ultrasonication on a mineral-free belt pressed cake.

Figure 9 shows the effect of ultrasonication on a high solids dry milled belt pressed cake.

Figure 10 shows the effect of ultrasonication on a high solids dry milled belt pressed cake.

Figures 11A, B and C show the effect of pressure level at various energy inputs of the sonication probe (sonicator) upon FLT index (a measure of tensile strength),  $d_{50}$  particle size of the microfibrillated cellulose and average power draw in the ultrasonic re-dispersing of microfibrillated cellulose and inorganic particulate material, which had been previously dried and pelletized and then reconstituted,

Figures 12A, B, and C show the effect of temperature level at various energy inputs of the sonication probe (sonicator) upon FLT index, viscosity and average power draw of the ultrasonic treatment, respectively, in the re-dispersing of microfibrillated cellulose and inorganic particulate material, which had been previously dried and pelletized and then reconstituted

Figures 13A and B show the effect of processing with a laboratory high shear mixer to make down previously dried, pelletized and reconstituted microfibrillated cellulose and

inorganic particulate material composition at different concentrations upon FLT index and

viscosity, respectively, before the application of ultrasonic re-dispersing of the microfibrillated and inorganic particulate material compositions at various energy inputs of the sonication probe (sonicator).

Figures 14A, B and C show the effect of continuous process of grinding a liquid slurry of cellulose fibres and inorganic particulate material to produce microfibrillated cellulose that has

never been dewatered or dried, followed by ultrasonic post-treatment processing of the slurry at various energy inputs and processing times of the sonication probe (sonicator), upon the FLT index,  $d_{50}$  particle size of the microfibrillated cellulose and average power draw of the sonication probe (sonicator), respectively, on two concentrations of microfibrillated cellulose and inorganic particulate material slurries.

Figures 15A, B and C show the effect of using a pulper and a refiner to re-disperse (make down) dried and pelletized microfibrillated cellulose and inorganic particulate material compositions at three different fibre solids contents, prior to treatment with a sonication probe (sonicator), upon FLT index, viscosity and  $d_{50}$  particle size of the microfibrillated cellulose, respectively.

Figures 16A and B show the post-treatment effect of sonication on microfibrillated cellulose compositions without inorganic particulate material that was produced, respectively by grinding in a stirred media detritor and by grinding in a stirred media detritor followed by passage through a homogenizer, then followed by ultrasonic treatment at various energy inputs, upon the FLT index and  $d_{50}$  particle size of the microfibrillated cellulose.

## Detailed Description

### The fibrous substrate comprising cellulose

**[0029]** The fibrous substrate comprising cellulose is derived from any suitable source, such as wood, grasses (e.g., sugarcane, bamboo) or rags (e.g., textile waste, cotton, hemp or flax). The fibrous substrate comprising cellulose is in the form of a pulp (i.e., a suspension of cellulose fibres in water), which is prepared by any suitable chemical or mechanical treatment, or combination thereof. For example, the pulp is a chemical pulp, or a chemithermomechanical pulp, or a mechanical pulp, or a recycled pulp, or a papermill broke, or a papermill waste stream, or waste from a papermill, or a combination thereof. The cellulose pulp is beaten (for example in a Valley beater) and/or otherwise refined (for example, processing in a conical or plate refiner) to any predetermined freeness, reported in the art as Canadian standard freeness (CSF) in  $\text{cm}^3$ . CSF means a value for the freeness or drainage rate of pulp measured by the rate that a suspension of pulp is drained. For example, the cellulose pulp has a Canadian standard freeness of about  $10 \text{ cm}^3$  or greater prior to being microfibrillated. The cellulose pulp has a CSF of about  $700 \text{ cm}^3$  or less, for example, equal to or less than about  $650 \text{ cm}^3$ , or equal to or less than about  $600 \text{ cm}^3$ , or equal to or less than about  $550 \text{ cm}^3$ , or equal to or less than about  $500 \text{ cm}^3$ , or equal to or less than about  $450 \text{ cm}^3$ , or equal to or less than about  $400 \text{ cm}^3$ , or equal to or less than about  $350 \text{ cm}^3$ , or equal to or less than about  $300$

cm<sup>3</sup>, or equal to or less than about 250 cm<sup>3</sup>, or equal to or less than about 200 cm<sup>3</sup>, or equal to or less than about 150 cm<sup>3</sup>, or equal to or less than about 100 cm<sup>3</sup>, or equal to or less than about 50 cm<sup>3</sup>. The cellulose pulp is then dewatered by methods well known in the art, for example, the pulp is filtered through a screen in order to obtain a wet sheet comprising at least about 10% solids, for example at least about 15% solids, or at least about 20% solids, or at least about 30% solids, or at least about 40% solids. The pulp is utilized in an unrefined state, that is to say, without being beaten or dewatered, or otherwise refined.

**[0030]** The fibrous substrate comprising cellulose is added to a grinding vessel or homogenizer in a dry state. For example, a dry paper broke is added directly to the grinder vessel. The aqueous environment in the grinder vessel will then facilitate the formation of a pulp.

#### **The inorganic particulate material**

**[0031]** The inorganic particulate material is, for example, be an alkaline earth metal carbonate or sulphate, such as calcium carbonate, magnesium carbonate, dolomite, gypsum, a hydrous kandite clay such as kaolin, halloysite or ball clay, an anhydrous (calcined) kandite clay such as metakaolin or fully calcined kaolin, talc, mica, perlite or diatomaceous earth, or magnesium hydroxide, or aluminium trihydrate, or combinations thereof.

**[0032]** A preferred inorganic particulate material for use in the method according to the present invention is calcium carbonate. Hereafter, the invention tends to be discussed in terms of calcium carbonate, and in relation to aspects where the calcium carbonate is processed and/or treated. The invention should not be construed as being limited to such embodiments.

**[0033]** The particulate calcium carbonate used in the present invention is obtained from a natural source by grinding. Ground calcium carbonate (GCC) is typically obtained by crushing and then grinding a mineral source such as chalk, marble or limestone, which is followed by a particle size classification step, in order to obtain a product having the desired degree of fineness. Alternatively, other techniques such as bleaching, flotation and magnetic separation are used to obtain a product having the desired degree of fineness and/or colour. The particulate solid material is ground autogenously, i.e. by attrition between the particles of the solid material themselves, or, alternatively, in the presence of a particulate grinding medium comprising particles of a different material from the calcium carbonate to be ground. These processes is carried out with or without the presence of a dispersant and biocides, which is added at any stage of the process. Precipitated calcium carbonate (PCC) is used as the source of particulate calcium carbonate in the present invention, and is produced by any of the known methods available in the art. TAPPI Monograph Series No 30, "Paper Coating Pigments", pages 34-35 describes the three main commercial processes for preparing precipitated calcium carbonate which is suitable for use in preparing products for use in the paper industry, but is also suitable to be used in the practice of the present invention. In all three processes, a

calcium carbonate feed material, such as limestone, is first calcined to produce quicklime, and the quicklime is then slaked in water to yield calcium hydroxide or milk of lime. In the first process, the milk of lime is directly carbonated with carbon dioxide gas. This process has the advantage that no by-product is formed, and it is relatively easy to control the properties and purity of the calcium carbonate product. In the second process the milk of lime is contacted with soda ash to produce, by double decomposition, a precipitate of calcium carbonate and a solution of sodium hydroxide. The sodium hydroxide is substantially completely separated from the calcium carbonate if this process is used commercially. In the third main commercial process the milk of lime is first contacted with ammonium chloride to give a calcium chloride solution and ammonia gas. The calcium chloride solution is then contacted with soda ash to produce by double decomposition precipitated calcium carbonate and a solution of sodium chloride. The crystals are produced in a variety of different shapes and sizes, depending on the specific reaction process that is used. The three main forms of PCC crystals are aragonite, rhombohedral and scalenohedral, all of which are suitable for use in the present invention, including mixtures thereof.

**[0034]** Wet grinding of calcium carbonate involves the formation of an aqueous suspension of the calcium carbonate which is optionally ground, optionally in the presence of a suitable dispersing agent. Reference is made to, for example, EP-A-614948 for more information regarding the wet grinding of calcium carbonate.

**[0035]** In some circumstances, minor additions of other minerals is included, for example, one or more of kaolin, calcined kaolin, wollastonite, bauxite, talc or mica, could also be present.

**[0036]** When the inorganic particulate material of the present invention is obtained from naturally occurring sources, it is that some mineral impurities will contaminate the ground material. For example, naturally occurring calcium carbonate is present in association with other minerals. Thus, in some embodiments, the inorganic particulate material includes an amount of impurities. In general, however, the inorganic particulate material used in the invention will *contain* less than about 5% by weight, preferably less than about 1% by weight, of other mineral impurities.

**[0037]** The inorganic particulate material used during a microfibrillating step will preferably have a particle size distribution in which at least about 10% by weight of the particles have an "equivalent spherical diameter" (e.s.d.) of less than 2 $\mu$ m, for example, at least about 20% by weight, or at least about 30% by weight, or at least about 40% by weight, or at least about 50% by weight, or at least about 60% by weight, or at least about 70% by weight, or at least about 80% by weight, or at least about 90% by weight, or at least about 95% by weight, or about 100% of the particles have an e.s.d. of less than 2 $\mu$ m.

**[0038]** Unless otherwise stated, particle size properties referred to herein for the inorganic particulate materials are as measured in a well-known manner by sedimentation of the particulate material in a fully dispersed condition in an aqueous medium using a Sedigraph 5100 machine as supplied by Micromeritics Instruments Corporation, Norcross, Georgia, USA

(telephone: +1 770 662 3620; web-site: [www.micromeritics.com](http://www.micromeritics.com)), referred to herein as a "Micromeritics Sedigraph 5100 unit." Such a machine provides measurements and a plot of the cumulative percentage by weight of particles having a size, referred to in the art as the "equivalent spherical diameter" (e.s.d.), less than given e.s.d. values. The mean particle size  $d_{50}$  is the value determined in this way of the particle e.s.d. at which there are 50% by weight of the particles which have an equivalent spherical diameter less than that  $d_{50}$  value. Alternatively, where stated, the particle size properties referred to herein for the inorganic particulate materials are as measured by the well-known conventional method employed in the art of laser light scattering, using a Malvern Mastersizer S machine as supplied by Malvern Instruments Ltd (or by other methods which give essentially the same result). In the laser light scattering technique, the size of particles in powders, suspensions and emulsions is measured using the diffraction of a laser beam, based on an application of Mie theory. Such a machine provides measurements and a plot of the cumulative percentage by volume of particles having a size, referred to in the art as the "equivalent spherical diameter" (e.s.d.), less than given e.s.d. values. The mean particle size  $d_{50}$  is the value determined in this way of the particle e.s.d. at which there are 50% by volume of the particles which have an equivalent spherical diameter less than that  $d_{50}$  value.

**[0039]** Alternatively, the inorganic particulate material used during a microfibrillating step will preferably have a particle size distribution, as measured using a Malvern Mastersizer S machine, in which at least about 10% by volume of the particles have an e.s.d. of less than  $2\mu\text{m}$ , for example, at least about 20% by volume, or at least about 30% by volume, or at least about 40% by volume, or at least about 50% by volume, or at least about 60% by volume, or at least about 70% by volume, or at least about 80% by volume, or at least about 90% by volume, or at least about 95% by volume, or about 100% of the particles by volume have an e.s.d. of less than  $2\mu\text{m}$ .

**[0040]** Unless otherwise stated, particle size properties of the microfibrillated cellulose materials are as measured by the well-known conventional method employed in the art of laser light scattering, using a Malvern Mastersizer S machine as supplied by Malvern Instruments Ltd (or by other methods which give essentially the same result).

**[0041]** Details of the procedure used to characterize the particle size distributions of mixtures of inorganic particle material and microfibrillated cellulose using a Malvern Mastersizer S machine are provided below.

**[0042]** Another preferred inorganic particulate material for use in the method according to the present invention is kaolin clay. Hereafter, this section of the specification tends to be discussed in terms of kaolin, and in relation to aspects where the kaolin is processed and/or treated. The invention should not be construed as being limited to such embodiments. Thus, in some embodiments, kaolin is used in an unprocessed form.

**[0043]** Kaolin clay used in this invention is a processed material derived from a natural source,

namely raw natural kaolin clay mineral. The processed kaolin clay typically contains at least about 50% by weight kaolinite. For example, most commercially processed kaolin clays contain greater than about 75% by weight kaolinite and contain greater than about 90%, in some cases greater than about 95% by weight of kaolinite.

**[0044]** Kaolin clay used in the present invention is prepared from the raw natural kaolin clay mineral by one or more other processes which are well known to those skilled in the art, for example by known refining or beneficiation steps.

**[0045]** For example, the clay mineral is bleached with a reductive bleaching agent, such as sodium hydrosulfite. If sodium hydrosulfite is used, the bleached clay mineral is optionally dewatered, and optionally washed and again optionally dewatered, after the sodium hydrosulfite bleaching step.

**[0046]** The clay mineral is treated to remove impurities, e.g., by flocculation, flotation, or magnetic separation techniques well known in the art. Alternatively the clay mineral used in the first aspect of the invention is untreated in the form of a solid or as an aqueous suspension.

**[0047]** The process for preparing the particulate kaolin clay used in the present invention optionally also includes one or more comminution steps, e.g., grinding or milling. Light comminution of a coarse kaolin is used to give suitable delamination thereof. The comminution is carried out by use of beads or granules of a plastic (e.g., nylon), sand or ceramic grinding or milling aid. The coarse kaolin is refined to remove impurities and improve physical properties using well known procedures. The kaolin clay is treated by a known particle size classification procedure, e.g., screening and centrifuging (or both), to obtain particles having a desired  $d_{50}$  value or particle size distribution.

#### **The microfibrillating process**

**[0048]** In accordance with the disclosure, there is provided a method of preparing a composition for use as a filler in paper or as a paper coating, comprising a step of microfibrillating a fibrous substrate comprising cellulose in the presence of an inorganic particulate material. According to particular embodiments of the present methods, the microfibrillating step is conducted in the presence of an inorganic particulate material which acts as a microfibrillating agent. By microfibrillating is meant a process in which microfibrils of cellulose are liberated or partially liberated as individual species or as smaller aggregates as compared to the fibres of the pre-microfibrillated pulp. Typical cellulose fibres (i.e., pre-microfibrillated pulp) suitable for use in papermaking include larger aggregates of hundreds or thousands of individual cellulose microfibrils. By microfibrillating the cellulose, particular characteristics and properties, including but not limited to the characteristic and properties described herein, are imparted to the microfibrillated cellulose and the compositions including the microfibrillated cellulose.

**[0049]** An exemplary microfibrillated cellulose prepared in accordance with the methods of the present disclosure is depicted in Figure 1. Figure 1 is a SEM micrograph of microfibrillated cellulose (having a  $d_{50}$  of 80  $\mu\text{m}$ ) prepared with GCC (60 wt% < 2 $\mu\text{m}$  particle size, by Sedigraph) at 5.0 % pulp on total dry weight. The media (Carbolite 16/20) volume concentration (MVC) was 50%. The energy input was 2500 kWh/t expressed on fibre. The step of microfibrillating is carried out in any suitable apparatus, including but not limited to a refiner. The microfibrillating step is conducted in a grinding vessel under wet-grinding conditions or the microfibrillating step is carried out in a homogenizer.

- ***wet-grinding***

**[0050]** The grinding is suitably performed in a conventional manner. The grinding is an attrition grinding process in the presence of a particulate grinding medium, or is an autogenous grinding process, i.e., one in the absence of a grinding medium. By grinding medium is meant a medium other than the inorganic particulate material which is co-ground with the fibrous substrate comprising cellulose.

**[0051]** The particulate grinding medium, when present, is of a natural or a synthetic material. The grinding medium, for example, comprises balls, beads or pellets of any hard mineral, ceramic or metallic material. Such materials includes, for example, alumina, zirconia, zirconium silicate, aluminium silicate or the mullite-rich material which is produced by calcining kaolinitic clay at a temperature in the range of from about 1300°C to about 1800°C. For example, in some embodiments a Carbolite® grinding media is preferred. Alternatively, particles of natural sand of a suitable particle size is used.

**[0052]** Generally, the type of and particle size of grinding medium to be selected for use in the invention is dependent on the properties, such as, e.g., the particle size of, and the chemical composition of, the feed suspension of material to be ground. Preferably, the particulate grinding medium comprises particles having an average diameter in the range of from about 0.1mm to about 6.0mm and, more preferably, in the range of from about 0.2mm to about 4.0mm. The grinding medium (or media) is present in an amount up to about 70% by volume of the charge. The grinding media is present in amount of at least about 10% by volume of the charge, for example, at least about 20 % by volume of the charge, or at least about 30% by volume of the charge, or at least about 40 % by volume of the charge, or at least about 50% by volume of the charge, or at least about 60 % by volume of the charge.

**[0053]** The grinding is carried out in one or more stages. For example, a coarse inorganic particulate material is ground in the grinder vessel to a predetermined particle size distribution, after which the fibrous material comprising cellulose is added and the grinding continued until the desired level of microfibrillation has been obtained. The coarse inorganic particulate material used in accordance with the first aspect of this invention initially for example has a particle size distribution in which less than about 20% by weight of the particles have an e.s.d.

of less than 2µm, for example, less than about 15% by weight, or less than about 10% by weight of the particles have an e.s.d. of less than 2µm. In another embodiment, the coarse inorganic particulate material used in accordance with this *invention* initially has a particle size distribution, as measured using a Malvern Mastersizer S machine, in which less than about 20% by volume of the particles have an e.s.d. of less than 2µm, for example, less than about 15% by volume, or less than about 1% by volume of the particles have an e.s.d. of less than 2µm.

**[0054]** The coarse inorganic particulate material is wet or dry ground in the absence or presence of a grinding medium. In the case of a wet grinding stage, the coarse inorganic particulate material is preferably ground in an aqueous suspension in the presence of a grinding medium. In such a suspension, the coarse inorganic particulate material preferably is present in an amount of from about 5% to about 85% by weight of the suspension; more preferably in an amount of from about 20% to about 80% by weight of the suspension. Most preferably, the coarse inorganic particulate material is present in an amount of about 30% to about 75% by weight of the suspension. As described above, the coarse inorganic particulate material is ground to a particle size distribution such that at least about 10% by weight of the particles have an e.s.d. of less than 2µm, for example, at least about 20% by weight, or at least about 30% by weight, or at least about 40% by weight, or at least about 50% by weight, or at least about 60% by weight, or at least about 70% by weight, or at least about 80% by weight, or at least about 90% by weight, or at least about 95% by weight, or about 100% by weight of the particles, have an e.s.d. of less than 2µm, after which the cellulose pulp is added and the two components are co-ground to microfibrillate the fibres of the cellulose pulp.

**[0055]** In another embodiment, the coarse inorganic particulate material is ground to a particle size distribution, as measured using a Malvern Mastersizer S machine such that at least about 10% by volume of the particles have an e.s.d. of less than 2µm, for example, at least about 20% by volume, or at least about 30% by volume or at least about 40% by volume, or at least about 50% by volume, or at least about 60% by volume, or at least about 70% by volume, or at least about 80% by volume, or at least about 90% by volume, or at least about 95% by volume, or about 100% by volume of the particles, have an e.s.d. of less than 2µm, after which the cellulose pulp is added and the two components are co-ground to microfibrillate the fibres of the cellulose pulp.

**[0056]** In one embodiment, the mean particle size ( $d_{50}$ ) of the inorganic particulate material is reduced during the co-grinding process. For example, the  $d_{50}$  of the inorganic particulate material is reduced by at least about 10% (as measured by a Malvern Mastersizer S machine), for example, the  $d_{50}$  of the inorganic particulate material is reduced by at least about 20%, or reduced by at least about 30%, or reduced by at least about 50%, or reduced by at least about 50%, or reduced by at least about 60%, or reduced by at least about 70%, or reduced by at least about 80%, or reduced by at least about 90%. For example, an inorganic particulate material having a  $d_{50}$  of 2.5 µm prior to co-grinding and a  $d_{50}$  of 1.5 µm post co-grinding will have been subject to a 40% reduction in particle size. In embodiments, the mean particle size

of the inorganic particulate material is not significantly reduced during the co-grinding process. By "not significantly reduced" is meant that the  $d_{50}$  of the inorganic particulate material is reduced by less than about 10%, for example, the  $d_{50}$  of the inorganic particulate material is reduced by less than about 5%.

**[0057]** The fibrous substrate comprising cellulose is microfibrillated in the presence of an inorganic particulate material to obtain microfibrillated cellulose having a  $d_{50}$  ranging from about 5 to  $\mu\text{m}$  about 500  $\mu\text{m}$ , as measured by laser light scattering. The fibrous substrate comprising cellulose is microfibrillated in the presence of an inorganic particulate material to obtain microfibrillated cellulose having a  $d_{50}$  of equal to or less than about 400  $\mu\text{m}$ , for example equal to or less than about 300  $\mu\text{m}$ , or equal to or less than about 200  $\mu\text{m}$ , or equal to or less than about 150  $\mu\text{m}$ , or equal to or less than about 125  $\mu\text{m}$ , or equal to or less than about 100  $\mu\text{m}$ , or equal to or less than about 90  $\mu\text{m}$ , or equal to or less than about 80  $\mu\text{m}$ , or equal to or less than about 70  $\mu\text{m}$ , or equal to or less than about 60  $\mu\text{m}$ , or equal to or less than about 50  $\mu\text{m}$ , or equal to or less than about 40  $\mu\text{m}$ , or equal to or less than about 30  $\mu\text{m}$ , or equal to or less than about 20  $\mu\text{m}$ , or equal to or less than about 10  $\mu\text{m}$ .

**[0058]** The fibrous substrate comprising cellulose is microfibrillated in the presence of an inorganic particulate material to obtain microfibrillated cellulose having a modal fibre particle size ranging from about 0.1-500  $\mu\text{m}$  and a modal inorganic particulate material particle size ranging from 0.25-20  $\mu\text{m}$ . The fibrous substrate comprising cellulose is microfibrillated in the presence of an inorganic particulate material to obtain microfibrillated cellulose having a modal fibre particle size of at least about 0.5  $\mu\text{m}$ , for example at least about 10  $\mu\text{m}$ , or at least about 50  $\mu\text{m}$ , or at least about 100  $\mu\text{m}$ , or at least about 150  $\mu\text{m}$ , or at least about 200  $\mu\text{m}$ , or at least about 300  $\mu\text{m}$ , or at least about 400  $\mu\text{m}$ .

**[0059]** The fibrous substrate comprising cellulose is microfibrillated in the presence of an inorganic particulate material to obtain microfibrillated cellulose having a fibre steepness equal to or greater than about 10, as measured by Malvern. Fibre steepness (i.e., the steepness of the particle size distribution of the fibres) is determined by the following formula:

$$\text{Steepness} = 100 \times (d_{30}/d_{70})$$

**[0060]** The microfibrillated cellulose for example has a fibre steepness equal to or less than about 100. The microfibrillated cellulose for example has a fibre steepness equal to or less than about 75, or equal to or less than about 50, or equal to or less than about 40, or equal to or less than about 30. The microfibrillated cellulose for example has a fibre steepness from about 20 to about 50, or from about 25 to about 40, or from about 25 to about 35, or from about 30 to about 40.

**[0061]** The grinding is suitably performed in a grinding vessel, such as a tumbling mill (e.g., rod, ball and autogenous), a stirred mill (e.g., SAM or IsaMill), a tower mill, a stirred media detritor (SMD), or a grinding vessel comprising rotating parallel grinding plates between which the feed to be ground is fed.

**[0062]** The grinding vessel is a tower mill. The tower mill comprises a quiescent zone above one or more grinding zones. A quiescent zone is a region located towards the top of the interior of tower mill in which minimal or no grinding takes place and comprises microfibrillated cellulose and inorganic particulate material. The quiescent zone is a region in which particles of the grinding medium sediment down into the one or more grinding zones of the tower mill.

**[0063]** The tower mill optionally comprises a classifier above one or more grinding zones. The classifier is top mounted and located adjacent to a quiescent zone. The classifier is for example a hydrocyclone. The tower mill optionally comprises a screen above one or more grind zones. A screen is located adjacent to a quiescent zone and/or a classifier. The screen is sized to separate grinding media from the product aqueous suspension comprising microfibrillated cellulose and inorganic particulate material and to enhance grinding media sedimentation.

**[0064]** The grinding is performed under plug flow conditions. Under plug flow conditions the flow through the tower is such that there is limited mixing of the grinding materials through the tower. This means that at different points along the length of the tower mill the viscosity of the aqueous environment will vary as the fineness of the microfibrillated cellulose increases. Thus, in effect, the grinding region in the tower mill is considered to comprise one or more grinding zones which have a characteristic viscosity. A skilled person in the art will understand that there is no sharp boundary between adjacent grinding zones with respect to viscosity.

**[0065]** Water is added at the top of the mill proximate to the quiescent zone or the classifier or the screen above one or more grinding zones to reduce the viscosity of the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material at those zones in the mill. By diluting the product microfibrillated cellulose and inorganic particulate material at this point in the mill it has been found that the prevention of grinding media carry over to the quiescent zone and/or the classifier and/or the screen is improved. Further, the limited mixing through the tower allows for processing at higher solids lower down the tower and dilute at the top with limited backflow of the dilution water back down the tower into the one or more grinding zones. Any suitable amount of water which is effective to dilute the viscosity of the product aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is added. The water is added continuously during the grinding process, or at regular intervals, or at irregular intervals.

**[0066]** Or, water is added to one or more grinding zones via one or more water injection points positioned along the length of the tower mill, or each water injection point being located at a position which corresponds to the one or more grinding zones. Advantageously, the ability to add water at various points along the tower allows for further adjustment of the grinding conditions at any or all positions along the mill. The tower mill optionally comprises a vertical impeller shaft equipped with a series of impeller rotor disks throughout its length. The action of the impeller rotor disks creates a series of discrete grinding zones throughout the mill.

**[0067]** Alternatively, the grinding is performed in a screened grinder, preferably a stirred media detritor. The screened grinder optionally comprises one or more screen(s) having a nominal aperture size of at least about 250  $\mu\text{m}$ , for example, the one or more screens have a nominal aperture size of at least about 300  $\mu\text{m}$ , or at least about 350 $\mu\text{m}$ , or at least about 400  $\mu\text{m}$ , or at least about 450  $\mu\text{m}$ , or at least about 500  $\mu\text{m}$ , or at least about 550  $\mu\text{m}$ , or at least about 600  $\mu\text{m}$ , or at least about 650  $\mu\text{m}$ , or at least about 700  $\mu\text{m}$ , or at least about 750  $\mu\text{m}$ , or at least about 800  $\mu\text{m}$ , or at least about 850  $\mu\text{m}$ , or at or least about 900  $\mu\text{m}$ , or at least about 1000  $\mu\text{m}$ .

**[0068]** The screen sizes noted immediately above are applicable to the tower mill embodiments described above.

**[0069]** As noted above, the grinding optionally is performed in the presence of a grinding medium. The grinding medium is a coarse media comprising particles having an average diameter in the range of from about 1 mm to about 6 mm, for example about 2 mm, or about 3 mm, or about 4 mm, or about 5 mm.

**[0070]** For example, the grinding media has a specific gravity of at least about 2.5, for example, at least about 3, or at least about 3.5, or at least about 4.0, or at least about 4.5, or least about 5.0, or at least about 5.5, or at least about 6.0.

**[0071]** Or, the grinding media comprises particles having an average diameter in the range of from about 1 mm to about 6 mm and has a specific gravity of at least about 2.5.

**[0072]** For example, the grinding media comprises particles having an average diameter of about 3 mm and specific gravity of about 2.7. As described above, the grinding medium (or media) is present in an amount up to about 70% by volume of the charge. The grinding media is present in amount of at least about 10% by volume of the charge, for example, at least about 20 % by volume of the charge, or at least about 30% by volume of the charge, or at least about 40 % by volume of the charge, or at least about 50% by volume of the charge, or at least about 60 % by volume of the charge. For example, the grinding medium is present in amount of about 50% by volume of the charge.

**[0073]** By "charge" is meant the composition which is the feed fed to the grinder vessel. The charge includes water, grinding media, and fibrous substrate comprising cellulose and inorganic particulate material, and any other optional additives as described herein.

**[0074]** The use of a relatively coarse and/or dense media has the advantage of improved (i.e., faster) sediment rates and reduced media carry over through the quiescent zone and/or classifier and/or screen(s).

**[0075]** A further advantage in using relatively coarse grinding media is that the mean particle size ( $d_{50}$ ) of the inorganic particulate material is not be significantly reduced during the grinding process such that the energy imparted to the grinding system is primarily expended in

microfibrillating the fibrous substrate comprising cellulose.

**[0076]** A further advantage in using relatively coarse screens is that a relatively coarse or dense grinding media is used in the microfibrillating step. In addition, the use of relatively coarse screens (i.e., having a nominal aperture of least about 250  $\mu\text{m}$ ) allows a relatively high solids product to be processed and removed from the grinder, which allows a relatively high solids feed (comprising fibrous substrate comprising cellulose and inorganic particulate material) to be processed in an economically viable process. As discussed below, it has been found that a feed having a high initial solids content is desirable in terms of energy sufficiency. Further, it has also been found that product produced (at a given energy) at lower solids has a coarser particle size distribution.

**[0077]** As discussed in the 'Background' section above, the present invention seeks to address the problem of preparing microfibrillated cellulose economically on an industrial scale.

**[0078]** Thus, the fibrous substrate comprising cellulose and inorganic particulate material are present in the aqueous environment at an initial solids content of at least about 4 wt. %, of which at least about 2 % by weight is fibrous substrate comprising cellulose. The initial solids content is for example at least about 10 wt. %, or at least about 20 wt. %, or at least about 30 wt. %, or at least about at least 40 wt. %. At least about 5 % by weight of the initial solids content is fibrous substrate comprising cellulose, for example, at least about 10 %, or at least about 15 %, or at least about 20 % by weight of the initial solids content is fibrous substrate comprising cellulose.

**[0079]** The grinding is performed in a cascade of grinding vessels, one or more of which comprise one or more grinding zones. For example, the fibrous substrate comprising cellulose and the inorganic particulate material is ground in a cascade of two or more grinding vessels, for example, a cascade of three or more grinding vessels, or a cascade of four or more grinding vessels, or a cascade of five or more grinding vessels, or a cascade of six or more grinding vessels, or a cascade of seven or more grinding vessels, or a cascade of eight or more grinding vessels, or a cascade of nine or more grinding vessels in series, or a cascade comprising up to ten grinding vessels. The cascade of grinding vessels is operatively linked in series or parallel or a combination of series and parallel. The output from and/or the input to one or more of the grinding vessels in the cascade is subjected to one or more screening steps and/or one or more classification steps.

**[0080]** The total energy expended in a microfibrillation process is for example apportioned equally across each of the grinding vessels in the cascade. Alternatively, the energy input optionally varies between some or all of the grinding vessels in the cascade.

**[0081]** A person skilled in the art will understand that the energy expended per vessel optionally varies between vessels in the cascade depending on the amount of fibrous substrate being microfibrillated in each vessel, and optionally the speed of grind in each vessel, the duration of grind in each vessel, the type of grinding media in each vessel and the type and

amount of inorganic particulate material. The grinding conditions is for example varied in each vessel in the cascade in order to control the particle size distribution of both the microfibrillated cellulose and the inorganic particulate material. For example, the grinding media size is varied between successive vessels in the cascade in order to reduce grinding of the inorganic particulate material and to target grinding of the fibrous substrate comprising cellulose.

**[0082]** The grinding is performed in a closed or the grinding is performed in an open circuit. The grinding is performed in batch mode or the grinding is performed in a re-circulating batch mode.

**[0083]** As described above, the grinding circuit optionally includes a pre-grinding step in which coarse inorganic particulate ground in a grinder vessel to a predetermined particle size distribution, after which fibrous material comprising cellulose is combined with the pre-ground inorganic particulate material and the grinding continued in the same or different grinding vessel until the desired level of microfibrillation has been obtained.

**[0084]** As the suspension of material to be ground is of a relatively high viscosity, a suitable dispersing agent is preferably added to the suspension prior to grinding. The dispersing agent is, for example, a water soluble condensed phosphate, polysilicic acid or a salt thereof, or a polyelectrolyte, for example a water soluble salt of a poly(acrylic acid) or of a poly(methacrylic acid) having a number average molecular weight not greater than 80,000. The amount of the dispersing agent used would generally be in the range of from 0.1 to 2.0% by weight, based on the weight of the dry inorganic particulate solid material. The suspension suitably is ground at a temperature in the range of from 4°C to 100°C. Other additives which are for example included during the microfibrillation step include: carboxymethyl cellulose, amphoteric carboxymethyl cellulose, oxidising agents, 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), TEMPO derivatives, and wood degrading enzymes.

**[0085]** The pH of the suspension of material to be ground is for example about 7 or greater than about 7 (i.e., basic), for example, the pH of the suspension is about 8, or about 9, or about 10, or about 11. The pH of the suspension of material to be ground is for example less than about 7 (i.e., acidic), for example, the pH of the suspension is about 6, or about 5, or about 4, or about 3. In an embodiment the pH of the suspension of material to be ground is adjusted by addition of an appropriate amount of acid or base. Suitable bases included alkali metal hydroxides, such as, for example NaOH. Other suitable bases are sodium carbonate and ammonia. Suitable acids included inorganic acids, such as hydrochloric and sulphuric acid, or organic acids. An exemplary acid is orthophosphoric acid.

**[0086]** The amount of inorganic particulate material and cellulose pulp in the mixture to be co-ground optionally varies in a ratio of from about 99.5:0.5 to about 0.5:99.5, based on the dry weight of inorganic particulate material and the amount of dry fibre in the pulp, for example, a ratio of from about 99.5:0.5 to about 50:50 based on the dry weight of inorganic particulate material and the amount of dry fibre in the pulp. For example, the ratio of the amount of inorganic particulate material and dry fibre is from about 99.5:0.5 to about 70:30. The ratio of

inorganic particulate material to dry fibre is about 80:20, or for example, about 85:15, or about 90:10, or about 91:9, or about 92:8, or about 93:7, or about 94:6, or about 95:5, or about 96:4, or about 97:3, or about 98:2, or about 99:1. Preferably, the weight ratio of inorganic particulate material to dry fibre is about 95:5. In another preferred embodiment, the weight ratio of inorganic particulate material to dry fibre is about 90:10, 85:15, 80:20 or 50:50.

**[0087]** The total energy input in a typical grinding process to obtain the desired aqueous suspension composition typically is between about 100 and 1500 kWh<sup>t</sup><sup>-1</sup> based on the total dry weight of the inorganic particulate filler. The total energy input is less than about 1000 kWh<sup>t</sup><sup>-1</sup>, for example, less than about 800 kWh<sup>t</sup><sup>-1</sup>, less than about 600 kWh<sup>t</sup><sup>-1</sup>, less than about 500 kWh<sup>t</sup><sup>-1</sup>, less than about 400 kWh<sup>t</sup><sup>-1</sup>, less than about 300 kWh<sup>t</sup><sup>-1</sup>, or less than about 200 kWh<sup>t</sup><sup>-1</sup>. As such, the present inventors have surprisingly found that a cellulose pulp is microfibrillated at relatively low energy input when it is co-ground in the presence of an inorganic particulate material. As will be apparent, the total energy input per tonne of dry fibre in the fibrous substrate comprising cellulose will be less than about 10,000 kWh<sup>t</sup><sup>-1</sup>, for example, less than about 9000 kWh<sup>t</sup><sup>-1</sup>, or less than about 8000 kWh<sup>t</sup><sup>-1</sup>, or less than about 7000 kWh<sup>t</sup><sup>-1</sup>, or less than about 6000 kWh<sup>t</sup><sup>-1</sup>, or less than about 5000 kWh<sup>t</sup><sup>-1</sup>, for example less than about 4000 kWh<sup>t</sup><sup>-1</sup>, less than about 3000 kWh<sup>t</sup><sup>-1</sup>, less than about 2000 kWh<sup>t</sup><sup>-1</sup>, less than about 1500 kWh<sup>t</sup><sup>-1</sup>, less than about 1200 kWh<sup>t</sup><sup>-1</sup>, less than about 1000 kWh<sup>t</sup><sup>-1</sup>, or less than about 800 kWh<sup>t</sup><sup>-1</sup>. The total energy input varies depending on the amount of dry fibre in the fibrous substrate being microfibrillated, and optionally the speed of grind and the duration of grind.

- ***homogenizing***

**[0088]** Microfibrillation of the fibrous substrate comprising cellulose is effected under wet conditions in the presence of the inorganic particulate material by a method in which the mixture of cellulose pulp and inorganic particulate material is pressurized (for example, to a pressure of about 500 bar) and then passed to a zone of lower pressure. The rate at which the mixture is passed to the low pressure zone is sufficiently high and the pressure of the low pressure zone is sufficiently low as to cause microfibrillation of the cellulose fibres. For example, the pressure drop is effected by forcing the mixture through an annular opening that has a narrow entrance orifice with a much larger exit orifice. The drastic decrease in pressure as the mixture accelerates into a larger volume (i.e., a lower pressure zone) induces cavitation which causes microfibrillation. In an embodiment, microfibrillation of the fibrous substrate comprising cellulose is effected in a homogenizer under wet conditions in the presence of the inorganic particulate material. In the homogenizer, the cellulose pulp-inorganic particulate material mixture is pressurized (for example, to a pressure of about 500 bar), and forced through a small nozzle or orifice. The mixture is pressurized to a pressure of from about 100 to about 1000 bar, for example to a pressure of equal to or greater than 300 bar, or equal to or greater than about 500, or equal to or greater than about 200 bar, or equal to or greater than about 700 bar. The homogenization subjects the fibres to high shear forces such that as the

pressurized cellulose pulp exits the nozzle or orifice, cavitation causes microfibrillation of the cellulose fibres in the pulp. In embodiments, additional water is added to improve flowability of the suspension through the homogenizer. The resulting aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is fed back into the inlet of the homogenizer for multiple passes through the homogenizer. Preferably, the inorganic particulate material is a naturally platy mineral, such as kaolin. As such, homogenization not only facilitates microfibrillation of the cellulose pulp, but also facilitates delamination of the platy particulate material.

**[0089]** A platy particulate material, such as kaolin, is understood to have a shape factor of at least about 10, for example, at least about 15, or at least about 20, or at least about 30, or at least about 40, or at least about 50, or at least about 60, or at least about 70, or at least about 80, or at least about 90, or at least about 100. Shape factor, as used herein, is a measure of the ratio of particle diameter to particle thickness for a population of particles of varying size and shape as measured using the electrical conductivity methods, apparatuses, and equations described in U.S. Patent No. 5,576,617.

**[0090]** A suspension of a platy inorganic particulate material, such as kaolin, is treated in the homogenizer to a predetermined particle size distribution in the absence of the fibrous substrate comprising cellulose, after which the fibrous material comprising cellulose is added to the aqueous slurry of inorganic particulate material and the combined suspension is processed in the homogenizer as described above. The homogenization process is continued, including one or more passes through the homogenizer, until the desired level of microfibrillation has been obtained. Similarly, the platy inorganic particulate material is treated in a grinder to a predetermined particle size distribution and then combined with the fibrous material comprising cellulose followed by processing in the homogenizer.

**[0091]** An exemplary homogenizer is a Manton Gaulin (APV) homogenizer.

**[0092]** After the microfibrillation step has been carried out, the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is screened to remove fibre above a certain size and to remove any grinding medium. For example, the suspension is subjected to screening using a sieve having a selected nominal aperture size in order to remove fibres which do not pass through the sieve. Nominal aperture size means the nominal central separation of opposite sides of a square aperture or the nominal diameter of a round aperture. The sieve is for example a BSS sieve (in accordance with BS 1796) having a nominal aperture size of 150µm, for example, a nominal aperture size 125µm, or 106µm, or 90µm, or 74µm, or 63µm, or 53µm, 45µm, or 38µm. In one embodiment, the aqueous suspension is screened using a BSS sieve having a nominal aperture of 125µm. The aqueous suspension is then optionally dewatered.

### **The aqueous suspension**

**[0093]** The aqueous suspensions produced in accordance with the methods described above are suitable for use in a method of making paper or coating paper. The aqueous suspension is suitable for use in a method of making paper or coating paper. The other optional additives include dispersant, biocide, suspending aids, salt(s) and other additives, for example, starch or carboxymethylcellulose or polymers, which facilitates the interaction of mineral particles and fibres during or after grinding.

**[0094]** The inorganic particulate material optionally have a particle size distribution such that at least about 10% by weight, for example at least about 20% by weight, for example at least about 30% by weight, for example at least about 40% by weight, for example at least about 50% by weight, for example at least about 60% by weight, for example at least about 70% by weight, for example at least about 80% by weight, for example at least about 90% by weight, for example at least about 95% by weight, or for example about 100% of the particles have an e.s.d. of less than 2µm.

**[0095]** The inorganic particulate material optionally have a particle size distribution, as measured by a Malvern Mastersizer S machine, such that at least about 10% by volume, for example at least about 20% by volume, for example at least about 30% by volume, for example at least about 40% by volume, for example at least about 50% by volume, for example at least about 60% by volume, for example at least about 70% by volume, for example at least about 80% by volume, for example at least about 90% by volume, for example at least about 95% by volume, or for example about 100% by volume of the particles have an e.s.d. of less than 2µm.

**[0096]** The amount of inorganic particulate material and cellulose pulp in the mixture to be co-ground varies in a ratio of from about 99.5:0.5 to about 0.5:99.5, based on the dry weight of inorganic particulate material and the amount of dry fibre in the pulp, for example, a ratio of from about 99.5:0.5 to about 50:50 based on the dry weight of inorganic particulate material and the amount of dry fibre in the pulp. For example, the ratio of the amount of inorganic particulate material and dry fibre is from about 99.5:0.5 to about 70:30, 80:20, 85:15, 90:10, 91:9, 92:8, 93:7, 94:6, 95:5, 96:4, 97:3, 98:2 or 99:1.

**[0097]** The weight ratio of inorganic particulate material to dry fibre is about 95:5, 90:10, 85:15, 80:20 or 50:50.

**[0098]** The composition does not include fibres too large to pass through a BSS sieve (in accordance with BS 1796) having a nominal aperture size of 150µm, for example, a nominal aperture size of 125µm, 106µm, or 90µm, or 74µm, or 63µm, or 53µm, 45µm, or 38µm.

**[0099]** It will be understood therefore that amount (i.e., % by weight) of microfibrillated cellulose in the aqueous suspension after grinding or homogenizing is less than the amount of dry fibre in the pulp if the ground or homogenized suspension is treated to remove fibres above a selected size. Thus, the relative amounts of pulp and inorganic particulate material fed to the grinder or homogenizer is adjusted depending on the amount of microfibrillated cellulose

that is required in the aqueous suspension after fibres above a selected size are removed.

**[0100]** The inorganic particulate material is an alkaline earth metal carbonate, for example, calcium carbonate. The inorganic particulate material is ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC), or a mixture of GCC and PCC. Or, the inorganic particulate material is a naturally platy mineral, for example, kaolin. Or, the inorganic particulate material is a mixture of kaolin and calcium carbonate, for example, a mixture of kaolin and GCC, or a mixture of kaolin and PCC, or a mixture of kaolin, GCC and PCC.

**[0101]** The aqueous suspension is treated to remove at least a portion or substantially all of the water to form a partially dried or essentially completely dried product. For example, at least about 10 % by volume of water in the aqueous suspension is removed from the aqueous suspension, for example, at least about 20% by volume, or at least about 30% by volume, or at least about 40% by volume, or at least about 50% by volume, or at least about 60% by volume, or at least about 70% by volume or at least about 80 % by volume or at least about 90% by volume, or at least about 100% by volume of water in the aqueous suspension is removed. Any suitable technique is used to remove water from the aqueous suspension including, for example, by gravity or vacuum-assisted drainage, with or without pressing, or by evaporation, or by filtration, or by a combination of these techniques. The partially dried or essentially completely dried product will comprise microfibrillated cellulose and inorganic particulate material and any other optional additives that have been added to the aqueous suspension prior to drying. The partially dried or essentially completely dried product is for example stored or packaged for sale. The partially dried or essentially completely dried product is optionally re-hydrated and incorporated in papermaking compositions and other paper products, as described herein.

### **The ultrasonication process**

**[0102]** In brief, sonication, ultrasonication or ultrasonification (herein used interchangeably unless otherwise noted) is the irradiation of a liquid sample with ultrasonic (>20 kHz. e.g., 20 to 100 kHz) sound waves which results in agitation of the liquid. The sound waves propagate into a liquid media resulting in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles or voids in the liquid, which then collapse violently (cavitation) during compression, creating very high local temperatures, and agitation. The combination of these events results in high shear forces capable of breaking down or reducing materials into smaller constituents essentially emulsifying the material. This process changes physical properties of the material depending on the operation parameters chosen.

**[0103]** Ultrasonication is used to re-disperse and de-agglomerate dewatered, partially dried or essentially dried microfibrillated cellulose containing compositions. The main applications of ultrasonics include homogenization (mixing), dispersing, de-agglomeration, wet-milling and grinding (e.g. nano-materials), emulsifying, and cell disintegration. Ultrasonication also aids in

mixing of materials through the agitation of the material. Although the present invention is not limited to the use of any particular sonication device, ultrasonication is most typically performed by use of an ultrasonic bath or an ultrasonic probe (or transducer). Suitable devices known in the art also include, and are not limited to an ultrasonic homogenizer, an ultrasonic foil and an ultrasonic horn. Commercial scale ultrasonication devices are available from Hielscher Ultrasonics GmbH (Oderstr. 53 D-14513 Teltow, Germany and 530 Ringwood Ave. Lembo & Gray Bldg. Wanaque, NJ 07465, USA). Suitable sonification probes are variously called sonotrodes and cascotrodes by the foregoing manufacturer

**[0104]** In trials reported in some of the Examples in this specification, a pilot scale ultrasonic probe (sonotrode) from Hielscher was utilized. In such trials, the unit was utilized with a 3L/min progressive cavity (seepex) pump.

**[0105]** In trials reported in certain Examples below, the trials were conducted in recirculation mode between the feed tank and the ultrasonic flow cell (this is where the sonication probe (sonotrode, *i.e.* the device that directs ultrasonic energy to the slurry, is located)). The starting volume in the feed tank for the reported trials was 2.5L. 250 ml samples were collected after 0, 1, 2, 4 and 10 min of sonication. The flow rate during all such trials was maintained at approximately 1.5 L/min. In addition, several processing configurations were possible using various combinations of boosters (B4-1.8 and B4-2.2) and sonotrodes (BS4d22 and BS4d40) to determine the configuration in the processing of various microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material feed products. Sonotrodes are used to directly transfer the ultrasonic energy generated by a transducer to the medium/slurry to be sonified. Boosters are used to mechanically increase (or decrease) the amplitude generated by sonotrodes.

**[0106]** Any effects of ultrasonication-induced cavitation on a material are controlled through a combination of parameters including different frequencies, displacement or vibration amplitudes, time of exposure to the process and mode of administration of the process (e.g., pulsed or continuous administration). Frequencies used typically range from about 20 to about 100 kHz, or from about 25 to about 55 kHz. Amplitudes used typically range from about 22 to about 50  $\mu\text{m}$ . Operating pressures of from 0 to 4 bar, preferably about 3 bar are utilized. Temperatures of 20°C to 50°C are suitable. Optimal conditions for sonification of slurries of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material were found to be 3 bar pressure, 20°C. and 1.5 wt.% fibre solids. The choice of using an ultrasonic bath, ultrasonic probe or other device also influences the end result of the process.

**[0107]** With regard to the present invention, it has been found that ultrasonication of the aqueous suspension comprising the microfibrillated cellulose or microfibrillated cellulose and an inorganic particulate material of the present invention (collectively referred to as the "aqueous suspension") enhances physical properties of the material. For example, ultrasonication of an aqueous suspension comprising microfibrillated cellulose or comprising microfibrillated cellulose and an inorganic particulate material surprisingly and unexpectedly results in enhanced viscosity and/or tensile strength of the material, as demonstrated in the

Examples section of this specification. The enhancement of the physical properties of the material of the present invention and the degree of enhancement is dependent upon the operating parameters used. In view of the teachings of this specification, one of ordinary skill in the art will be able to discern the parameters appropriate to achieve a desired result without undue experimentation.

**[0108]** In an aspect of the present invention, the ultrasonication of the aqueous suspension of the present invention comprises producing a sonicated suspension comprising microfibrillated cellulose and inorganic particulate material with enhanced viscosity and/or tensile strength properties, the method comprising a step of microfibrillating a fibrous substrate comprising cellulose in an aqueous environment in the presence of an inorganic particulate material to produce an aqueous suspension comprising microfibrillated cellulose and inorganic particulate material, and further comprising subjecting the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material to sonication to produce the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material with enhanced viscosity and tensile strength properties. The microfibrillating step optionally comprises grinding the fibrous substrate comprising cellulose in the presence of the inorganic particulate material and optionally further comprise an initial step of grinding the inorganic particulate material in the absence of the fibrous substrate comprising cellulose to obtain an inorganic particulate material having a desired particle size.

**[0109]** In one embodiment, a grinding media, as discussed above, is also used to produce the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material with enhanced viscosity and tensile strength properties.

**[0110]** Ultrasonication of the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is conducted with an ultrasonic probe or ultrasonic water bath, an ultrasonic homogenizer, an ultrasonic foil or an ultrasonic horn. The use of such devices is known to one of ordinary skill in the art.

**[0111]** In an embodiment of the present invention, the methods of the present invention further comprises one or more of high shear mixing, homogenisation or refining either before or after the sonication step, all of which are known by one of ordinary skill in the art and is incorporated into the methods of the present invention without undue experimentation in view of the teachings of this specification.

**Re-Dispersion of Dewatered, Partially Dried or Essentially Dried Microfibrillated Cellulose Compositions, Optionally Containing Inorganic Particulate Material.**

**[0112]** In the present invention, ultrasonication is advantageously used to re-disperse previously dewatered, partially dried or essentially dried compositions of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material. The dewatered partially dried or essentially dried compositions of microfibrillated cellulose or

compositions of microfibrillated cellulose and inorganic particulate material is for example pelletized after dewatering and drying. Such dewatered, partially dried or essentially dried, and optionally pelletized, compositions of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material are re-suspended with the aid of ultrasonication devices of the types described in this specification.

**[0113]** In an embodiment ultrasonication is used as a post-treatment step for slurries of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material to improve one or more physical property of such slurries, for example, increased tensile strength and enhanced viscosity.

**[0114]** In an embodiment, the inventors have invented a method for re-dispersing dewatered, partially dried or essentially dried microfibrillated cellulose, according to claim 1.

**[0115]** The method comprises a second outlet of the flow cell connected to a second inlet of the tank, thereby providing for a continuous recirculation loop providing for the continuous application of ultrasonic energy to the slurry for a desired time period and/or total energy input range. Thus, the method is practiced in a continuous manner by recirculating a slurry comprising microfibrillated cellulose or a slurry comprising microfibrillated cellulose and at least one inorganic particulate material through the above-described recirculation loop comprising the flow cell comprising at least one sonication probe. In a preferred embodiment, the dispersing liquid is water.

**[0116]** In an embodiment, the cumulative ultrasonic energy input is adjusted to at least about 200 kWh/t, at least about 300 kWh/t, at least about 400 kWh/t, at least about 500 kWh/t, at least about 600 kWh/t, at least about 700 kWh/t, at least about 800 kWh/t, at least about 900 kWh/t, at least about 1,000 kWh/t, at least about 1,100 kWh/t, at least about 1,200 kWh/t, at least about 1,300 kWh/t, at least about 1,400 kWh/t, at least about 1,500 kWh/t, at least about 1,600 kWh/t, at least about 1,700 kWh/t, at least about 1,750 kWh/t, at least about 1,800 kWh/t, at least about 1,900 kWh/t, at least about 2,000 kWh/t, at least about 2,100 kWh/t, at least about 2,200 kWh/t, at least about 2,300 kWh/t, at least about 2,400 kWh/t, at least about 2,500 kWh/t, at least about 3,000 kWh/t, at least about 3,500 kWh/t, at least about 4,000 kWh/t, at least about 4,500 kWh/t, at least about 5,000 kWh/t, at least about 5,500 kWh/t, at least about 6,000 kWh/t, at least about 6,500 kWh/t, at least about 7,000 kWh/t, at least about 7,500 kWh/t, at least about 8,000 kWh/t, at least about 8,500 kWh/t, at least about 9,000 kWh/t, at least about 9,500 kWh/t, or at least about 10,000 kWh/t.

**[0117]** In an embodiment, the flow cell comprises a cooling jacket for maintaining a temperature of the suspension of microfibrillated cellulose in the range of about 1° C to about 80° C., 20° C to about 50° C., or at room temperature, or about 20° C.

**[0118]** The flow cell comprises an adjustable valve at the second outlet to create back pressure of the recirculated liquid of from 0 to 4 bar,

**[0119]** In an embodiment, flow cell further comprises one or more boosters to mechanically increase or decrease the amplitude of the at least one sonication probe. The person skilled in the art will understand how boosters are used to adjust the amplitude of the ultrasonic energy emitted from the sonication probe.

**[0120]** The liquid composition, preferably an aqueous slurry, is of from 0.5 to 5%, or about 1.5% fibre solids, or about 1.6% fibre solids, or about 1.7% fibre solids, or about 1.8% fibre solids, or about 1.9% fibre solids, or about 2% fibre solids, or about 2.5% fibre solids, or about 3% fibre solids, or about 3.5% fibre solids, or about 4% fibre solids, or about 4.5, or about 5% fibre solids.

**[0121]** In some embodiments, the microfibrillated cellulose composition is pelletized.

**[0122]** In other embodiments, the microfibrillated cellulose composition comprising inorganic particulate material is pelletized.

**[0123]** The ultrasonic energy is applied for about 1 to about 120 minutes, or about 30 minutes, or about 45 minutes, or about 60 minutes, or about 75 minutes, or about 90 minutes, or about 120 minutes.

**[0124]** In an embodiment, the recirculation loop further comprises a high shear mixer.

**[0125]** The person skilled in the art will understand that improvements in tensile strength of the suspension of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material are demonstrated by the FLT index previously described in this specification.

**[0126]** In an embodiment, the improvement in FLT index in suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material made by the methods described in this specification employing ultrasonic treatment of such suspensions compared to suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material which were not made by the methods described in this specification employing ultrasonic treatment of such suspensions. FLT indices of 7.5 Nm/g or more, of 7.5 Nm/g or more, of 8 Nm/g or more, of 8.5 Nm/g or more, of 9 Nm/g or more, of 9.5 Nm/g or more, of 10 Nm/g or more, of 10.5 Nm/g or more, of 11 Nm/g or more, of 11.5 Nm/g or more, of 12 Nm/g or more, of 12.5 Nm/g or more, of 13 Nm/g or more, of 13.5 Nm/g or more, of 14 Nm/g or more, of 14.5 Nm/g or more, or of 15 Nm/g or more are achievable through the methods disclosed in the specification.

**[0127]** In an embodiment improvements in FLT index of about 5%, about 6%, about 7%, about 7.5%, about 8%, about 9%, about 10%, about 12.5%, about 15% or about 20% or more are achieved.

**[0128]** In an embodiment improvements in viscosity of about 5%, about 6%, about 7%, about 7.5%, about 8%, about 9%, about 10%, about 12.5% , about 15% or about 20% or more are

achieved compared to suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material produced without the application of ultrasonic energy treatment to the slurry or suspension.

**[0129]** In an embodiment, the liquid composition comprising microfibrillation cellulose is recirculated for about 30 to about 120 minutes, or about 30 to about 90 minutes, or about 30 to about 75 minutes, or about 30 to about 60 minutes, or about 30 to about 45 minutes, or about 30 minutes.

**[0130]** In an embodiment, the method further comprises one or more of high shear mixing, homogenization and refining either before or after the sonication step.

**[0131]** The sonification step of the process is carried out with at least one sonication probe (sonotrode) contained within a flow cell comprising forming part of a closed recirculation loop. The closed recirculation loop comprises a closed tank for adding a suitable dispersing liquid, preferably water. The tank is connected to an inlet to a suitable pump. An outlet of the pump is connected to an inlet to the flow cell comprising the at least one sonotrode. The outlet of the flow cell is connected by a tube to a second inlet to the closed mixing tank, thereby creating a recirculating loop for recirculation of the liquid composition comprising microfibrillated cellulose and optionally at least one inorganic particulate material.

**[0132]** In certain embodiments, the liquid composition of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material contains other optional additives. The optional additives could be, for example, a retention aid, or other additives used in papermaking compositions, for example, a sizing agent which is, for example, a long chain alkylketene dimer, a wax emulsion or a succinic acid derivative. The composition optionally also contains dye and/or an optical brightening agent. The composition optionally also comprises dry and wet strength aids such as, for example, starch or epichlorhydrin copolymers. Other optional additives include dispersant, biocide, suspending aids, salt(s) and other additives, for example, starch or carboxymethylcellulose or polymers, which facilitates the interaction of mineral particles and fibres during or after grinding.

**[0133]** The liquid composition of microfibrillated cellulose, an optionally at least one or more inorganic particulate material, is continuously recirculated through the recirculation loop. During recirculation of the liquid composition of microfibrillated cellulose, and optionally at least one or more inorganic particulate material, ultrasonic energy is applied through an ultrasonication device. In a preferred embodiment, the ultrasonication device is a sonotrode is well known in the art. Exemplary sonotrodes are available from, for example, Hielscher Ultrasonics GmbH (Oderstr. 53 D-14513 Teltow, Germany and 530 Ringwood Ave. Lembo & Gray Bldg. Wanaque, NJ 07465, USA).

**[0134]** Ultrasonic energy is applied continuously by the sonication probe (sonotrode) housed within the flow cell. Ultrasonic energy is applied in an cumulative amount of at least about 200 kWh/t, at least about 300 kWh/t, at least about 400 kWh/t, at least about 500 kWh/t, at least

about 600 kWh/t, at least about 700 kWh/t, at least about 800 kWh/t, at least about 900 kWh/t, at least about 1,000 kWh/t, at least about 1,100 kWh/t, at least about 1,200 kWh/t, at least about 1,300 kWh/t, at least about 1,400 kWh/t, at least about 1,500 kWh/t, at least about 1,600 kWh/t, at least about 1,700 kWh/t, at least about 1,750 kWh/t, at least about 1,800 kWh/t, at least about 1,900 kWh/t, at least about 2,000 kWh/t, at least about 2,100 kWh/t, at least about 2,200 kWh/t, at least about 2,300 kWh/t, at least about 2,400 kWh/t, at least about 2,500 kWh/t, at least about 3,000 kWh/t, at least about 3,500 kWh/t, at least about 4,000 kWh/t, at least about 4,500 kWh/t, at least about 5,000 kWh/t, at least about 5,500 kWh/t, at least about 6,000 kWh/t, at least about 6,500 kWh/t, at least about 7,000 kWh/t, at least about 7,500 kWh/t, at least about 8,000 kWh/t, at least about 8,500 kWh/t, at least about 9,000 kWh/t, at least about 9,500 kWh/t, or at least about 10,000 kWh/t.

**[0135]** In an embodiment, the flow cell comprises a cooling jacket for maintaining a temperature of the suspension of microfibrillated cellulose in the range of about 1° C to about 80° C. , or about 20° C to about 50°, or at room temperature, or preferably about 20° C.

**[0136]** In the invention, the flow cell comprises an adjustable valve at the second outlet to create back pressure of the recirculated liquid of from 0 to 4 bar, preferably about 3 bar.

**[0137]** In an embodiment, flow cell further comprises one or more boosters to mechanically increase or decrease the amplitude of the at least one sonication probe. The person skilled in the art will understand how boosters are used to adjust the amplitude of the ultrasonic energy emitted from the sonication probe.

**[0138]** In the invention, the liquid composition, preferably an aqueous slurry, is at 0.5% to 5% solids, or about 1.5% fibre solids, or about 1.6% fibre solids, or about 1.7% fibre solids, or about 1.8% fibre solids, or about 1.9% fibre solids, or about 2% fibre solids, or about 2.5% fibre solids, or about 3% fibre solids, or about 3.5% fibre solids, or about 4% fibre solids, or about 4.5, or about 5% fibre solids.

**[0139]** In the invention, ultrasonication is advantageously used to re-disperse previously dewatered, partially dried or essentially dried compositions of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material. The dewatered, partially dried or essentially dried compositions of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material are for example pelletized after dewatering and drying. Such dewatered, partially dried or dried, and optionally pelletized, compositions of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material are re-suspended with the aid of ultrasonication devices of the types described in this specification.

**[0140]** In the invention, the ultrasonic energy is applied for about 1 to about 120 minutes, or about 30 minutes, or about 45 minutes, or about 60 minutes, or about 75 minutes, or about 90 minutes, or about 120 minutes.

**[0141]** The person skilled in the art will understand that improvements in tensile strength of the suspension of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material is demonstrated by the FLT index previously described in this specification.

**[0142]** In an embodiment, the improvement in FLT index in suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material made by the methods described in this specification employing ultrasonic treatment of such suspensions compared to suspensions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material which were not made by the methods described in this specification employing ultrasonic treatment of such suspensions. FLT indices of 7.5 Nm/g or more, of 7.5 Nm/g or more, of 8 Nm/g or more, of 8.5 Nm/g or more, of 9 Nm/g or more, of 9.5 Nm/g or more, of 10 Nm/g or more, of 10.5 Nm/g or more, of 11 Nm/g or more, of 11.5 Nm/g or more, of 12 Nm/g or more, of 12.5 Nm/g or more, of 13 Nm/g or more, of 13.5 Nm/g or more, of 14 Nm/g or more, of 14.5 Nm/g or more, or of 15 Nm/g or more, are achievable through the methods disclosed in the specification.

**[0143]** In an embodiment of the present invention, the tensile strength of the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material with enhanced viscosity and tensile strength properties is increased by at least 5%, at least 10%, at least 20%, at least 50%, at least 100% or at least 200% over the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material not subject to sonication.

**[0144]** In an embodiment of the present invention, the viscosity of the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material with enhanced viscosity and tensile strength properties is increased by at least 5%, at least by 10% or at least by 20%, by at least 50%, by at least 100% over the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material not subject to sonication.

**[0145]** In an embodiment of the present invention, the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is subject to sonication for at least 30 seconds, at least 1 minute, at least 2 minutes, at least 5 minutes, at least 10 minutes and at least 20 minutes or longer. The length of time is determined by one of ordinary skill in the art based on the teachings of this specification.

**[0146]** In an embodiment of the present invention, the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is subject to sonication at an energy compensation rate of up to 1000 kwh per tonne of dried fibrils, up to 2000 kwh per tonne, 2500 kwh per tonne of dried fibrils, up to 5000 kwh per tonne of dried fibrils and up to 10000 kwh per tonne of dried fibrils. As set forth in the Examples of this application, sonication was found to be more effective for re-dispersing and de-agglomerating microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material that had been dewatered, partially dried, or essentially dried and pelletized. In other embodiments, re-dispersion of slurries of slurries of microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material through sonication yielded improvements in product quality at

energy inputs between 200 kWh/t and 10,000 kWh/t, especially between 1000 kWh/t and 2000 kWh/t.

**[0147]** In an embodiment, sonication of mineral free microfibrillated cellulose (e.g., birch) produced using the a pilot scale stirred media detritor (Supermill) yielded products with comparable specifications to microfibrillated cellulose made by grinding processes in, for example a Supermill, followed by a homogenization step when sonicated at about 1500 kWh/t.

**[0148]** In certain embodiments, the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is sonicated by running the sonicator in continuous mode.

**[0149]** In preferred embodiments, the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is formed into a semi (partially)-dry product prior to sonication. A belt pressed cake is one example of a semi-dried product suitable for use in the present invention. In certain embodiments, the belt press cake is further subjected to treatment in an air swept dryer and mill, such as an Atritor dryer. Often converting the product to a semi-dry product is done, for example, for ease of handling and/or transport. In the event of using a semi-dried product as a starting material, sonication not only provides enhanced physical properties to the material but also aids in disbursement of the material into solution in a process referred to as rewetting.

**[0150]** The sonication of the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is not limited to any particular or specific sonication parameters as a change on one parameter compensates for a change in another parameter, within physical and practical limits of the equipment and material being sonicated. For example, lengthening sonication time compensates at least partly for using a reduced amplitude.

**[0151]** In the invention, the sonication is performed at an amplitude of up to 60%, up to 80%, up to 100% and up to 200% or more, to the physical limitations of the sonicator used. Said upper physical limits of amplitude of a particular device used are known to one of ordinary skill in the art.

**[0152]** The fibrous substrate comprising cellulose is in the form of a pulp, for example, a chemical pulp, or a chemithermomechanical pulp, or a mechanical pulp, or a recycled pulp, or a paper broke pulp, or a papermill waste stream, or waste from a papermill, or combinations thereof.

**[0153]** The inorganic particulate material is an alkaline earth metal carbonate or sulphate, such as calcium carbonate, magnesium carbonate, dolomite, gypsum, a hydrous kandite clay such as kaolin, halloysite or ball clay, an anhydrous (calcined) kandite clay such as metakaolin or fully calcined kaolin, talc, mica, perlite or diatomaceous earth, or combinations thereof. In a preferred embodiment, the inorganic particulate material is an alkaline earth metal carbonate, for example, calcium carbonate or kaolin or a combination thereof.

**[0154]** The grinding vessel is for example a tower mill or a stirred media detritor.

**[0155]** In an embodiment, the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material with enhanced viscosity and tensile strength properties obtained by the method of the present invention is suitable for use in a method of making paper or coating paper and is suitable for other use in other processes and materials where microfibrillated cellulose is typically used, examples of which are detailed below in the section entitled "Other Uses."

**[0156]** In another aspect of the invention, the cellulose suspension is produced without the use of an inorganic particulate material. In these instances, a grinding media, as discussed above and below, is used in place of the inorganic particulate material. In this regard, the ultrasonication of the cellulose suspension of the present invention comprises producing an aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties, the method comprising a step of microfibrillating a fibrous substrate comprising cellulose in an aqueous environment to produce an aqueous suspension comprising microfibrillated cellulose, and further comprising subjecting the aqueous suspension comprising microfibrillated cellulose to sonication to produce the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties. The microfibrillating step optionally comprises grinding the fibrous substrate comprising cellulose in the presence of a grinding media, the grinding media having a desired particle size. The grinding media is for example partially or completely removed after the microfibrillating step.

**[0157]** Ultrasonication of the aqueous suspension comprising microfibrillated cellulose is conducted with an ultrasonic probe or ultrasonic water bath, an ultrasonic homogenizer, an ultrasonic foil or an ultrasonic horn. The use of such devices is known to one of ordinary skill in the art.

**[0158]** Such probes are known to one of ordinary skill in the art. In view of the teachings of this specification, one of ordinary skill in the art will be able to discern the appropriate parameters without undue experimentation.

**[0159]** In an embodiment of the present invention, the methods of the present invention further comprises one or more of high shear mixing, homogenisation or refining either before or after the sonication step, all of which are known by one of ordinary skill in the art and is incorporated into the methods of the present invention without undue experimentation in view of the teachings of this specification.

**[0160]** In an embodiment of the present invention, the tensile strength of the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties is increased by at least 5%, at least 10%, at least 20%, at least 50%, at least 100% or at least 200% over the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material not subject to sonication.

**[0161]** In an embodiment of the present invention, the viscosity of the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties is increased by at least 5%, at least by 10% or at least by 20%, by at least 50%, by at least 100% over the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material not subject to sonication.

**[0162]** In an embodiment of the present invention, the aqueous suspension comprising microfibrillated cellulose is subject to sonication for at least 30 seconds, at least 1 minute, at least 2 minutes, at least 3 minutes, at least 4 minutes, at least 5 minutes, at least 10 minutes and at least 20 minutes or longer. The length of time is determined by one of ordinary skill in the art based on the teachings of this specification.

**[0163]** In an embodiment of the present invention, the aqueous suspension comprising microfibrillated cellulose is subject to sonication at an energy compensation rate of up to 1000 kwh per tonne of dried fibrils, up to 1500 kwh per tonne, up to 2000 kwh per tonne, up to 2500 kwh per tonne of dried fibrils, up to 5000 kwh per tonne of dried fibrils and up to 10000 kwh per tonne of dried fibrils.

**[0164]** The aqueous suspension comprising microfibrillated cellulose and, optionally inorganic particulate material, is sonicated by running the sonicator in continuous mode or in pulse mode or a combination of both. That is, where alternating long pulses and short pulses are performed as desired patterns or at random.

**[0165]** The aqueous suspension comprising microfibrillated cellulose and, optionally inorganic particulate material, is formed into a semi (partially)-dry product prior to sonication. A belt pressed cake is one example of a semi-dried product suitable for use in the present invention. Another embodiment is a belt pressed cake followed by further drying in an air swept mill such as an Attritor dryer mill. Often converting the product to a semi-dry product is done, for example, for ease of handling and/or transport. In the event of using a semi-dried product as a starting material, sonication not only provides enhanced physical properties to the material but also aids in disbursement of the material into solution or suspension.

**[0166]** The sonication of the aqueous suspension comprising microfibrillated cellulose and, optionally inorganic particulate material, is not limited to any particular or specific sonication parameters as a change on one parameter compensates for a change in another parameter, within physical and practical limits. For example, lengthening sonication time compensates at least partly for a reduced amplitude.

**[0167]** In the invention, the sonication is performed at an amplitude of up to 60%, up to 80%, up to 100% and up to 200% or more, to the physical limitations of the sonicator used. Said upper physical limits of amplitude of a particular device used are known to one of ordinary skill in the art.

**[0168]** The fibrous substrate comprising cellulose is in the form of a pulp, for example, a chemical pulp, or a chemithermomechanical pulp, or a mechanical pulp, or a recycled pulp, or a paper broke pulp, or a papermill waste stream, or waste from a papermill, or combinations thereof.

**[0169]** In an embodiment, the aqueous suspension comprising microfibrillated cellulose and, optionally, inorganic particulate material with enhanced viscosity and tensile strength properties obtained by the method of the present invention is suitable for use in a method of making paper or coating paper and is suitable for other use in other processes and materials where microfibrillated cellulose is typically used and is suitable for other use in other processes and materials where microfibrillated cellulose is typically used, examples of which are detailed below in the section entitled "Other Uses."

#### **Paper products and processes for preparing same**

**[0170]** The aqueous suspension comprising microfibrillated cellulose and inorganic particulate material is for example incorporated in papermaking compositions, which in turn are used to prepare paper products. The term paper product, as used in connection with the present invention, should be understood to mean all forms of paper, including board such as, for example, white-lined board and linerboard, cardboard, paperboard, coated board, and the like. There are numerous types of paper, coated or uncoated, which are made according to the present invention, including paper suitable for books, magazines, newspapers and the like, and office papers. The paper is calendered or super calendered as appropriate; for example super calendered magazine paper for rotogravure and offset printing is made according to the present methods. Paper suitable for light weight coating (LWC), medium weight coating (MWC) or machine finished pigmentisation (MFP) is also made according to the present methods.

**[0171]** Coated paper and board having barrier properties suitable for food packaging and the like is also made according to the present methods. In a typical papermaking process, a cellulose-containing pulp is prepared by any suitable chemical or mechanical treatment, or combination thereof, which are well known in the art. The pulp is derived from any suitable source such as wood, grasses (e.g., sugarcane, bamboo) or rags (e.g., textile waste, cotton, hemp or flax). The pulp is bleached in accordance with processes which are well known to those skilled in the art and those processes suitable for use in the present invention will be readily evident. The bleached cellulose pulp is beaten, refined, or both, to a predetermined freeness (reported in the art as Canadian standard freeness

**[0172]** (CSF) in cm<sup>3</sup>). A suitable paper stock is then prepared from the bleached and beaten pulp.

**[0173]** The papermaking composition typically comprises, in addition to the aqueous suspension of microfibrillated cellulose and inorganic particulate material, paper stock and

other conventional additives known in the art. The papermaking composition optionally comprises up to about 50% by weight inorganic particulate material derived from the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material based on the total dry contents of the papermaking composition. For example, the papermaking composition comprises at least about 2% by weight, or at least about 5% by weight, or at least about 10% by weight, or at least about 15% by weight, or at least about 20% by weight, or at least about 25% by weight, or at least about 30% by weight, or at least about 35% by weight, or at least about 40% by weight, or at least about 45% by weight, or at least about 50% by weight, or at least about 60% by weight, or at least about 70% by weight, or at least about 80% by weight of inorganic particulate material derived from the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material based on the total dry contents of the papermaking composition. The microfibrillated cellulose material optionally has a fibre steepness of greater than about 10, for examples, from about 20 to about 50, or from about 25 to about 40, or from about 25 to 35, or from about 30 to about 40. The papermaking composition for example also contains a non-ionic, cationic or an anionic retention aid or microparticle retention system in an amount in the range from about 0.1 to 2% by weight, based on the dry weight of the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material. It optionally also contains a sizing agent which is, for example, a long chain alkylketene dimer, a wax emulsion or a succinic acid derivative. The composition optionally also contains dye and/or an optical brightening agent. The composition optionally also comprises dry and wet strength aids such as, for example, starch or epichlorhydrin copolymers.

**[0174]** The present disclosure is directed to a process for making a paper product comprising: (i) obtaining or preparing a fibrous substrate comprising cellulose in the form of a pulp suitable for making a paper product; (ii) preparing a papermaking composition from the pulp in step (i), the aqueous suspension of this invention comprising microfibrillated cellulose and inorganic particulate material, and other optional additives (such as, for example, a retention aid, and other additives such as those described above); and (iii) forming a paper product from said papermaking composition.

**[0175]** As noted above, the step of forming a pulp for example takes place in the grinder vessel or homogenizer by addition of the fibrous substrate comprising cellulose in a dry state, for example, in the form of a dry paper broke or waste, directly to the grinder vessel. The aqueous environment in the grinder vessel or homogenizer will then facilitate the formation of a pulp.

**[0176]** An additional filler component (i.e., a filler component other than the inorganic particulate material which is co-ground with the fibrous substrate comprising cellulose) is added to the papermaking composition prepared in step (ii). Exemplary filler components are PCC, GCC, kaolin, or mixtures thereof. An exemplary PCC is scalenohedral PCC. The weight ratio of the inorganic particulate material to the additional filler component in the papermaking composition is from about 1:1 to about 1:30, for example, from about 1:1 to about 1:20, for example, from about 1:1 to about 1:15, for example from about 1:1 to about 1:10, for example

from about 1:1 to about 1:7, for example, from about 1:3 to about 1:6, or about 1:1, or about 1:2, or about 1:3, or about 1:4, or about 1:5. Paper products made from such papermaking compositions exhibit greater strength compared to paper products comprising only inorganic particulate material, such as for example PCC, as filler. Paper products made from such papermaking compositions exhibit greater strength compared to a paper product in which inorganic particulate material and a fibrous substrate comprising cellulose are prepared (e.g., ground) separately and are admixed to form a paper making composition. Equally, paper products prepared from a papermaking composition according to the present disclosure exhibit a strength which is comparable to paper products comprising less inorganic particulate material. In other words, paper products is prepared from a paper making composition according to the present at higher filler loadings without loss of strength.

**[0177]** The steps in the formation of a final paper product from a papermaking composition are conventional and well known in the art and generally comprise the formation of paper sheets having a targeted basis weight, depending on the type of paper being made.

**[0178]** Additional economic benefits are achieved

**[0179]** in that the cellulose substrate for making the aqueous suspension are derived from the same cellulose pulp formed for making the papermaking composition and the final paper product. As such, the present disclosure is directed to a an integrated process for making a paper product comprising: (i) obtaining or preparing a fibrous substrate comprising cellulose in the form of a pulp suitable for making a paper product; (ii) microfibrillating a portion of said fibrous substrate comprising cellulose in accordance with the first aspect of the invention to prepare an aqueous suspension comprising microfibrillated cellulose and inorganic particulate material; (iii) preparing a papermaking composition from the pulp in step (i), the aqueous suspension prepared in step (ii), and other optional additives; and iv) forming a paper product from said papermaking composition.

**[0180]** Thus, since the cellulose substrate for preparing the aqueous suspension has already been prepared for the purpose of making the papermaking compositions, the step of forming the aqueous suspension does not necessarily require a separate step of preparing the fibrous substrate comprising cellulose.

**[0181]** Paper products prepared using the aqueous suspension of the present disclosure have surprisingly been found to exhibit improved physical and mechanical properties whilst at the same time enabling the inorganic particulate material to be incorporated at relatively high loading levels. Thus, improved papers are prepared at relatively less cost. For example, paper products prepared from papermaking compositions comprising the aqueous suspension of the present disclosure have been found to exhibit improved retention of the inorganic particulate material filler compared to paper products which do not contain any microfibrillated cellulose. Paper products prepared from papermaking compositions comprising the aqueous suspension of the present disclosure have also been found to exhibit improved burst strength and tensile strength. Further, the incorporation of the microfibrillated cellulose has been found to reduce

porosity compared to paper comprising the same amount of filler but no microfibrillated cellulose. This is advantageous since high filler loading levels are generally associated with relatively high values of porosity and are detrimental to printability.

#### **Paper coating composition and coating process**

**[0182]** The aqueous suspension of the present disclosure is used as a coating composition without the addition of further additives. However, optionally, a small amount of thickener such as carboxymethylcellulose or alkali-swelling acrylic thickeners or associated thickeners is added.

**[0183]** The coating composition contains one or more optional additional components, if desired. Such additional components, where present, are suitably selected from known additives for paper coating compositions. Some of these optional additives provides more than one function in the coating composition. Examples of known classes of optional additives are as follows:

1. (a) one or more additional pigments: the compositions described herein is used as sole pigments in the paper coating compositions, or is used in conjunction with one another or with other known pigments, such as, for example, calcium sulphate, satin white, and so-called "plastic pigment". When a mixture of pigments is used, the total pigment solids content is preferably present in the composition in an amount of at least about 75 wt. % of the total weight of the dry components of the coating composition;
2. (b) one or more binding or co-binding agents: for example, latex, which are, optionally, carboxylated, including: a styrene-butadiene rubber latex; an acrylic polymer latex; a polyvinyl acetate latex; or a styrene acrylic copolymer latex, starch derivatives, sodium carboxymethyl cellulose, polyvinyl alcohol, and proteins;
3. (c) one or more cross linkers: for example, in levels of up to about 5% by weight; e.g., glyoxals, melamine formaldehyde resins, ammonium zirconium carbonates; one or more dry or wet pick improvement additives: e.g., in levels up to about 2% by weight, e.g., melamine resin, polyethylene emulsions, urea formaldehyde, melamine formaldehyde, polyamide, calcium stearate, styrene maleic anhydride and others; one or more dry or wet rub improvement and abrasion resistance additives: e.g., in levels up to about 2% by weight, e.g., glyoxal based resins, oxidised polyethylenes, melamine resins, urea formaldehyde, melamine formaldehyde, polyethylene wax, calcium stearate and others; one or more water resistance additives: e.g., in levels up to about 2% by weight, e.g., oxidised polyethylenes, ketone resin, anionic latex, polyurethane, SMA, glyoxals, melamine resin, urea formaldehyde, melamine formaldehyde, polyamide, stearates and other materials commercially available for this function;
4. (d) one or more water retention aids: for example, in levels up to about 2% by weight, e.g., sodium carboxymethyl cellulose, hydroxyethyl cellulose, PVOH (polyvinyl alcohol), starches, proteins, polyacrylates, gums, alginates, polyacrylamide bentonite and other commercially available products sold for such applications;

5. (e) one or more viscosity modifiers and/or thickeners: for example, in levels up to about 2% by weight; e.g., acrylic associative thickeners, polyacrylates, emulsion copolymers, dicyanamide, triols, polyoxyethylene ether, urea, sulphated castor oil, polyvinyl pyrrolidone, CMC (carboxymethyl celluloses, for example sodium carboxymethylcellulose), sodium alginate, xanthan gum, sodium silicate, acrylic acid copolymers, HMC (hydroxymethylcelluloses), HEC (hydroxyethylcelluloses) and others;
6. (f) one or more lubricity/calendering aids: for example, in levels up to about 2% by weight, e.g., calcium stearate, ammonium stearate, zinc stearate, wax emulsions, waxes, alkyl ketene dimer, glycols; one or more gloss-ink hold-out additives: e.g., in levels up to about 2% by weight, e.g., oxidised polyethylenes, polyethylene emulsions, waxes, casein, guar gum, CMC, HMC, calcium stearate, ammonium stearate, sodium alginate and others;
7. (g) one or more dispersants: the dispersant is a chemical additive capable, when present in a sufficient amount, of acting on the particles of the particulate inorganic material to prevent or effectively restrict flocculation or agglomeration of the particles to a desired extent, according to normal processing requirements. The dispersant is present in levels up to about 1% by weight, and includes, for example, polyelectrolytes such as polyacrylates and copolymers containing polyacrylate species, especially polyacrylate salts (e.g., sodium and aluminium optionally with a group II metal salt), sodium hexametaphosphates, non-ionic polyol, polyphosphoric acid, condensed sodium phosphate, non-ionic surfactants, alkanolamine and other reagents commonly used for this function. The dispersants are, for example, selected from conventional dispersant materials commonly used in the processing and grinding of inorganic particulate materials. Such dispersants will be well recognized by those skilled in this art. They are generally water-soluble salts capable of supplying anionic species which in their effective amounts adsorb on the surface of the inorganic particles and thereby inhibit aggregation of the particles. The unsolvated salts suitably include alkali metal cations such as sodium. Solvation is in some cases assisted by making the aqueous suspension slightly alkaline. Examples of suitable dispersants include: water soluble condensed phosphates, e.g., polymetaphosphate salts [general form of the sodium salts:  $(\text{NaPO}_3)_x$ ] such as tetrasodium metaphosphate or so-called "sodium hexametaphosphate" (Graham's salt); water-soluble salts of polysilicic acids; polyelectrolytes; salts of homopolymers or copolymers of acrylic acid or methacrylic acid, or salts of polymers of other derivatives of acrylic acid, suitably having a weight average molecular mass of less than about 20,000. Sodium hexametaphosphate and sodium polyacrylate, the latter suitably having a weight average molecular mass in the range of about 1,500 to about 10,000, are especially preferred;
8. (h) one or more antifoamers and defoamers: for example, in levels up to about 1 % by weight, e.g., blends of surfactants, tributyl phosphate, fatty polyoxyethylene esters plus fatty alcohols, fatty acid soaps, silicone emulsions and other silicone containing compositions, waxes and inorganic particulates in mineral oil, blends of emulsified hydrocarbons and other compounds sold commercially to carry out this function;
9. (i) one or more optical brightening agents (OBA) and fluorescent whitening agents (FWA): for example, in levels up to about 1 % by weight, e.g., stilbene derivatives;

10. (j) one or more dyes: for example, in levels up to about 0.5% by weight;
11. (k) one or more biocides/spoilage control agents: for example, in levels up to about 1 % by weight, e.g., oxidizing biocides such as chlorine gas, chlorine dioxide gas, sodium hypochlorite, sodium hypobromite, hydrogen, peroxide, peracetic oxide, ammonium bromide/sodium hypochlorite, or non-oxidising biocides such as GLUT (Glutaraldehyde, CAS No 90045-36-6), ISO (CIT/MIT) (Isothiazolinone, CAS Np 55956-84-9 & 96118-96-6), ISO (BIT/MIT) (Isothiazolinone), ISO (BIT) (Isothiazolinone, CAS No 2634-33-5), DBNPA, BNPD (Bronopol), NaOPP, CARBAMATE, THIONE (Dazomet), EDDM - dimethanol (0-formal), HT - Triazine (N-formal), THPS - tetrakis (0-formal), TMAD - diurea (N-formal), metaborate, sodium dodecylbenene sulphonate, thiocyanate, organosulphur, sodium benzoate and other compounds sold commercially for this function, e.g., the range of biocide polymers sold by Nalco;
12. (l) one or more levelling and evening aids: for example, in levels up to about 2% by weight, e.g., non-ionic polyol, polyethylene emulsions, fatty acid, esters and alcohol derivatives, alcohol/ethylene oxide, calcium stearate and other compounds sold commercially for this function;
13. (m) one or more grease and oil resistance additives: for example, in levels up to about 2% by weight, e.g., oxidised polyethylenes, latex, SMA (styrene maleic anhydride), polyamide, waxes, alginate, protein, CMC, and HMC.

**[0184]** Any of the above additives and additive types is used alone or in admixture with each other and with other additives, if desired.

**[0185]** For all of the above additives, the percentages by weight quoted are based on the dry weight of inorganic particulate material (100%) present in the composition. Where the additive is present in a minimum amount, the minimum amount is about 0.01% by weight based on the dry weight of pigment.

**[0186]** The coating process is carried out using standard techniques which are well known to the skilled person. The coating process optionally also involves calendaring or supercalendering the coated product.

**[0187]** Methods of coating paper and other sheet materials, and apparatus for performing the methods, are widely published and well known. Such known methods and apparatus conveniently are used for preparing coated paper. For example, there is a review of such methods published in Pulp and Paper International, May 1994, page 18 et seq. Sheets are coated on the sheet forming machine, i.e., "on-machine" or "off-machine" on a coater or coating machine. Use of high solids compositions is desirable in the coating method because it leaves less water to evaporate subsequently. However, as is well known in the art, the solids level should not be so high that high viscosity and leveling problems are introduced. The methods of coating are performed using an apparatus comprising (i) an application for applying the coating composition to the material to be coated and (ii) a metering device for

ensuring that a correct level of coating composition is applied. When an excess of coating composition is applied to the applicator, the metering device is downstream of it. Alternatively, the correct amount of coating composition is applied to the applicator by the metering device, e.g., as a film press. At the points of coating application and metering, the paper web support ranges from a backing roll, e.g., via one or two applicators, to nothing (i.e., just tension}. The time the coating is in contact with the paper before the excess is finally removed is the dwell time - and this is short, long or variable.

**[0188]** The coating is usually added by a coating head at a coating station. According to the quality desired, paper grades are uncoated, single-coated, double-coated and even triple-coated. When providing more than one coat, the initial coat (pre-coat) optionally has a cheaper formulation and optionally coarser pigment in the coating composition. A coater that is applying coating on each side of the paper will have two or four coating heads, depending on the number of coating layers applied on each side. Most coating heads coat only one side at a time, but some roll coaters (e.g., film presses, gate rolls, and size presses} coat both sides in one pass.

**[0189]** Examples of known coaters which are employed include, without limitation, air knife coaters, blade coaters, rod coaters, bar coaters, multi-head coaters, roll coaters, roll or blade coaters, cast coaters, laboratory coaters, gravure coaters, kisscoaters, liquid application systems, reverse roll coaters, curtain coaters, spray coaters and extrusion coaters.

**[0190]** Water is added to the solids comprising the coating composition to give a concentration of solids which is preferably such that, when the composition is coated onto a sheet to a desired target coating weight, the composition has a rheology which is suitable to enable the composition to be coated with a pressure (i.e., a blade pressure) of between 1 and 1.5 bar.

**[0191]** Calendering is a well-known process in which paper smoothness and gloss is improved and bulk is reduced by passing a coated paper sheet between calender nips or rollers one or more times. Usually, elastomer-coated rolls are employed to give pressing of high solids compositions. In embodiments, an elevated temperature is applied. In embosiments, one or more (e.g., up to about 12, or sometimes higher) passes through the nips is applied.

**[0192]** Coated paper products prepared in accordance with the present disclosure and which contain optical brightening agent in the coating exhibit a brightness as measured according to ISO Standard 11475 which is at least 2 units greater, for example at least 3 units greater compared to a coated paper product which does not comprise microfibrillated cellulose which has been prepared in accordance with the present disclosure.

**[0193]** Coated paper products prepared in accordance with the present disclosure exhibit a Parker Print Surf smoothness measured according to ISO standard 8971-4 (1992) which is at least 0.5  $\mu\text{m}$  smoother, for example at least about 0.6  $\mu\text{m}$  smoother, or at least about 0.7  $\mu\text{m}$  smoother compared to a coated paper product which does not comprise microfibrillated cellulose which has been prepared in accordance with the present disclosure.

**Microfibrillation in the absence of grindable inorganic particulate material**

**[0194]** In another aspect, the present disclosure is directed to a method for preparing an aqueous suspension comprising microfibrillated cellulose, the method comprising a step of microfibrillating a fibrous substrate comprising cellulose in an aqueous environment by grinding in the presence of a grinding medium which is to be removed after the completion of grinding, wherein the grinding is performed in a tower mill or a screened grinder, and wherein the grinding is carried out in the absence of grindable inorganic particulate material.

**[0195]** A grindable inorganic particulate material is a material which would be ground in the presence of the grinding medium.

**[0196]** The particulate grinding medium is of a natural or a synthetic material. The grinding medium, for example, comprises balls, beads or pellets of any hard mineral, ceramic or metallic material. Such materials include, for example, alumina, zirconia, zirconium silicate, aluminium silicate or the mullite-rich material which is produced by calcining kaolinitic clay at a temperature in the range of from about 1300°C to about 1800°C. For example, in some embodiments a Carbolite® grinding media is preferred. Alternatively, particles of natural sand of a suitable particle size is used.

**[0197]** Generally, the type of and particle size of grinding medium to be selected for use in the invention is dependent on the properties, such as, e.g., the particle size of, and the chemical composition of, the feed suspension of material to be ground. Preferably, the particulate grinding medium comprises particles having an average diameter in the range of from about 0.5 mm to about 6 mm. In one embodiment, the particles have an average diameter of at least about 3 mm.

**[0198]** The grinding medium for example comprises particles having a specific gravity of at least about 2.5. The grinding medium for example comprises particles have a specific gravity of at least about 3, or least about 4, or least about 5, or at least about 6 .

**[0199]** The grinding medium (or media) is present in an amount up to about 70% by volume of the charge. The grinding media is present in amount of at least about 10% by volume of the charge, for example, at least about 20 % by volume of the charge, or at least about 30% by volume of the charge, or at least about 40 % by volume of the charge, or at least about 50% by volume of the charge, or at least about 60 % by volume of the charge.

**[0200]** The fibrous substrate comprising cellulose is for example microfibrillated to obtain microfibrillated cellulose having a  $d_{50}$  ranging from about 5 to  $\mu\text{m}$  about 500  $\mu\text{m}$ , as measured by laser light scattering. The fibrous substrate comprising cellulose is for example microfibrillated to obtain microfibrillated cellulose having a  $d_{50}$  of equal to or less than about 400  $\mu\text{m}$ , for example equal to or less than about 300  $\mu\text{m}$ , or equal to or less than about 200

µm, or equal to or less than about 150 µm, or equal to or less than about 125 µm, or equal to or less than about 100 µm, or equal to or less than about 90 µm, or equal to or less than about 80 µm, or equal to or less than about 70 µm, or equal to or less than about 60 µm, or equal to or less than about 50 µm, or equal to or less than about 40 µm, or equal to or less than about 30 µm, or equal to or less than about 20 µm, or equal to or less than about 10 µm.

**[0201]** The fibrous substrate comprising cellulose is for example microfibrillated to obtain microfibrillated cellulose having a modal fibre particle size ranging from about 0.1-500 µm. The fibrous substrate comprising cellulose is for example microfibrillated in the presence to obtain microfibrillated cellulose having a modal fibre particle size of at least about 0.5 µm, for example at least about 10 µm, or at least about 50 µm, or at least about 100 µm, or at least about 150 µm, or at least about 200 µm, or at least about 300 µm, or at least about 400 µm.

**[0202]** The fibrous substrate comprising cellulose is microfibrillated to obtain microfibrillated cellulose having a fibre steepness equal to or greater than about 10, as measured by Malvern. Fibre steepness (i.e., the steepness of the particle size distribution of the fibres) is determined by the following formula:  
Steepness =  $100 \times (d_{30}/d_{70})$

**[0203]** The microfibrillated cellulose for example has a fibre steepness equal to or less than about 100. The microfibrillated cellulose for example has a fibre steepness equal to or less than about 75, or equal to or less than about 50, or equal to or less than about 40, or equal to or less than about 30. The microfibrillated cellulose for example has a fibre steepness from about 20 to about 50, or from about 25 to about 40, or from about 25 to about 35, or from about 30 to about 40.

**[0204]** In one embodiment, the grinding vessel is a tower mill. The tower mill optionally comprises a quiescent zone above one or more grinding zones. A quiescent zone is a region located towards the top of the interior of a tower mill in which minimal or no grinding takes place and comprises microfibrillated cellulose and inorganic particulate material. The quiescent zone is a region in which particles of the grinding medium sediment down into the one or more grinding zones of the tower mill.

**[0205]** The tower mill optionally comprises a classifier above one or more grinding zones. In an embodiment, the classifier is top mounted and located adjacent to a quiescent zone. The classifier is for example a hydrocyclone.

**[0206]** The tower mill optionally comprises a screen above one or more grind zones. In an embodiment, a screen is located adjacent to a quiescent zone and/or a classifier. The screen is sized to separate grinding media from the product aqueous suspension comprising microfibrillated cellulose and to enhance grinding media sedimentation.

**[0207]** The grinding is performed under plug flow conditions. Under plug flow conditions the

flow through the tower is such that there is limited mixing of the grinding materials through the tower. This means that at different points along the length of the tower mill the viscosity of the aqueous environment will vary as the fineness of the microfibrillated cellulose increases. Thus, in effect, the grinding region in the tower mill is considered to comprise one or more grinding zones which have a characteristic

**[0208]** viscosity. A skilled person in the art will understand that there is no sharp boundary between adjacent grinding zones with respect to viscosity.

**[0209]** Water is added at the top of the mill proximate to the quiescent zone or the classifier or the screen above one or more grinding zones to reduce the viscosity of the aqueous suspension comprising microfibrillated cellulose at those zones in the mill. By diluting the product microfibrillated cellulose at this point in the mill it has been found that the prevention of grinding media carry over to the quiescent zone and/or the classifier and/or the screen is improved. Further, the limited mixing through the tower allows for processing at higher solids lower down the tower and dilute at the top with limited backflow of the dilution water back down the tower into the one or more grinding zones. Any suitable amount of water which is effective to dilute the viscosity of the product aqueous suspension comprising microfibrillated cellulose is added. The water is added continuously during the grinding process, or at regular intervals, or at irregular intervals.

**[0210]** Water is added to one or more grinding zones via one or more water injection points positioned along the length of the tower mill, the or each water injection point being located at a position which corresponds to the one or more grinding zones. Advantageously, the ability to add water at various points along the tower allows for further adjustment of the grinding conditions at any or all positions along the mill. The tower mill optionally comprises a vertical impeller shaft equipped with a series of impeller rotor disks throughout its length. The action of the impeller rotor disks creates a series of discrete grinding zones throughout the mill.

**[0211]** The grinding is performed in a screened grinder, preferably a stirred media detritor. The screened grinder optionally comprises one or more screen(s) having a nominal aperture size of at least about 250  $\mu\text{m}$ , for example, the one or more screens have a nominal aperture size of at least about 300  $\mu\text{m}$ , or at least about 350  $\mu\text{m}$ , or at least about 400  $\mu\text{m}$ , or at least about 450  $\mu\text{m}$ , or at least about 500  $\mu\text{m}$ , or at least about 550  $\mu\text{m}$ , or at least about 600  $\mu\text{m}$ , or at least about 650  $\mu\text{m}$ , or at least about 700  $\mu\text{m}$ , or at least about 750  $\mu\text{m}$ , or at least about 800  $\mu\text{m}$ , or at least about 850  $\mu\text{m}$ , or at or least about 900  $\mu\text{m}$ , or at least about 1000  $\mu\text{m}$ .

**[0212]** The screen sizes noted immediately above are applicable to the tower mill embodiments described above.

**[0213]** As noted above, the grinding is performed in the presence of a grinding medium. In an embodiment, the grinding medium is a coarse media comprising particles having an average diameter in the range of from about 1 mm to about 6 mm, for example about 2 mm, or about 3 mm, or about 4 mm, or about 5 mm.

**[0214]** The grinding media has a specific gravity of at least about 2.5 for example, at least about 3, or at least about 3.5, or at least about 4.0, or at least about 4.5, or at least about 5.0, or at least about 5.5, or at least about 6.0.

**[0215]** As described above, the grinding medium (or media) is in an amount up to about 70% by volume of the charge. The grinding media is present in amount of at least about 10% by volume of the charge, for example, at least about 20 % by volume of the charge, or at least about 30% by volume of the charge, or at least about 40 % by volume of the charge, or at least about 50% by volume of the charge, or at least about 60 % by volume of the charge.

**[0216]** The grinding medium is present in amount of about 50% by volume of the charge. By 'charge' is meant the composition which is the feed fed to the grinder vessel. The charge includes water, grinding media, the fibrous substrate comprising cellulose and any other optional additives (other than as described herein).

**[0217]** The use of a relatively coarse and/or dense media has the advantage of improved (i.e., faster) sediment rates and reduced media carry over through the quiescent zone and/or classifier and/or screen(s).

**[0218]** A further advantage in using relatively coarse screens is that a relatively coarse or dense grinding media can be used in the microfibrillating step. In addition, the use of relatively coarse screens (i.e., having a nominal aperture of least about 250  $\mu\text{m}$ ) allows a relatively high solids product to be processed and removed from the grinder, which allows a relatively high solids feed (comprising fibrous substrate comprising cellulose and inorganic particulate material) to be processed in an economically viable process. As discussed below, it has been found that a feed having a high initial solids content is desirable in terms of energy sufficiency. Further, it has also been found that product produced (at a given energy) at lower solids has a coarser particle size distribution.

**[0219]** As discussed in the 'Background' section above, the present invention seeks to address the problem of preparing microfibrillated cellulose economically on an industrial scale. Thus, the fibrous substrate comprising cellulose is present in the aqueous environment at an initial solids content of at least about 1 wt %. The fibrous substrate comprising cellulose is present in the aqueous environment at an initial solids content of at least about 2 wt %, for example at least about 3 wt %, or at least about at least 4 wt %. Typically the initial solids content will be no more than about 10 wt%.

**[0220]** The grinding is performed in a cascade of grinding vessels, one or more of which optionally comprise one or more grinding zones. For example, the fibrous substrate comprising cellulose is ground in a cascade of two or more grinding vessels, for example, a cascade of three or more grinding vessels, or a cascade of four or more grinding vessels, or a cascade of five or more grinding vessels, or a cascade of six or more grinding vessels, or a cascade of seven or more grinding vessels, or a cascade of eight or more grinding vessels, or a cascade

of nine or more grinding vessels in series, or a cascade comprising up to ten grinding vessels. The cascade of grinding vessels is operatively inked in series or parallel or a combination of series and parallel. The output from and/or the input to one or more of the grinding vessels in the cascade is subjected to one or more screening steps and/or one or more classification steps.

**[0221]** The total energy expended in a microfibrillation process is for example apportioned equally across each of the grinding vessels in the cascade. Alternatively, the energy input varies between some or all of the grinding vessels in the cascade.

**[0222]** A person skilled in the art will understand that the energy expended per vessel varies between vessels in the cascade depending on the amount of fibrous substrate being microfibrillated in each vessel, and optionally the speed of grind in each vessel, the duration of grind in each vessel and the type of grinding media in each vessel. The grinding conditions is for example varied in each vessel in the cascade in order to control the particle size distribution of the microfibrillated cellulose.

**[0223]** The grinding is performed in a closed circuit or the grinding is performed in an open circuit.

**[0224]** As the suspension of material to be ground is of a relatively high viscosity, a suitable dispersing agent preferably is added to the suspension prior to grinding. The dispersing agent is, for example, a water soluble condensed phosphate, polysilicic acid or a salt thereof, or a polyelectrolyte, for example a water soluble salt of a poly(acrylic acid) or of a poly(methacrylic acid) having a number average molecular weight not greater than 80,000. The amount of the dispersing agent used would generally be in the range of from 0.1 to 2.0% by weight, based on the weight of the dry inorganic particulate solid material. The suspension suitably is ground at a temperature in the range of from 4 °C to 100°C. Other additives which are for example included during the microfibrillation step include: carboxymethyl cellulose, amphoteric carboxymethyl cellulose, oxidising agents, 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), TEMPO derivatives, and wood degrading enzymes.

**[0225]** The pH of the suspension of material to be ground is about 7 or greater than about 7 (i.e., basic), for example, the pH of the suspension be about 8, or about 9, or about 10, or about 11. Alternatively, the pH of the suspension of material to be ground is less than about 7 (i.e., acidic), for example, the pH of the suspension is about 6, or about 5, or about 4, or about 3. The pH of the suspension of material to be ground is adjusted by addition of an appropriate amount of acid or base. Suitable bases included alkali metal hydroxides, such as, for example NaOH. other suitable bases are sodium carbonate and ammonia. Suitable acids included inorganic acids, such as hydrochloric and sulphuric acid, or organic acids. An exemplary acid is orthophosphoric acid.

**[0226]** The total energy input in a typical grinding process to obtain the desired aqueous suspension composition typically is between about 100 and 1500 kWh<sup>t</sup><sup>-1</sup> based on the total dry

weight of the inorganic particulate filler. The total energy input is for example less than about  $1000 \text{ kWh t}^{-1}$ , for example, less than about  $800 \text{ kWh t}^{-1}$ , less than about  $600 \text{ kWh t}^{-1}$ , less than about  $500 \text{ kWh t}^{-1}$ , less than about  $400 \text{ kWh t}^{-1}$ , less than about  $300 \text{ kWh t}^{-1}$ , or less than about  $200 \text{ kWh t}^{-1}$ . As such, the present inventors have surprisingly found that a cellulose pulp is microfibrillated at relatively low energy input when it is co-ground in the presence of an inorganic particulate material. As will be apparent, the total energy input per tonne of dry fibre in the fibrous substrate comprising cellulose will be less than about  $10,000 \text{ kWh t}^{-1}$ , for example, less than about  $9000 \text{ kWh t}^{-1}$ , or less than about  $8000 \text{ kWh t}^{-1}$ , or less than about  $7000 \text{ kWh t}^{-1}$ , or less than about  $6000 \text{ kWh t}^{-1}$ , or less than about  $5000 \text{ kWh t}^{-1}$ . for example less than about  $4000 \text{ kWh t}^{-1}$ , less than about  $3000 \text{ kWh t}^{-1}$ , less than about  $2000 \text{ kWh t}^{-1}$ , less than about  $1500 \text{ kWh t}^{-1}$ , less than about  $1200 \text{ kWh t}^{-1}$ , less than about  $1000 \text{ kWh t}^{-1}$ , or less than about  $800 \text{ kWh t}^{-1}$ . The total energy input varies depending on the amount of dry fibre in the fibrous substrate being microfibrillated, and optionally the speed of grind and the duration of grind.

**[0227]** With regard to the present invention, it has been found that ultrasonication of the aqueous suspension comprising microfibrillated cellulose (collectively referred to as the "aqueous suspension") enhances physical properties of the material. For example, ultrasonication of an aqueous suspension comprising microfibrillated cellulose surprisingly and unexpectedly results in enhanced viscosity and/or tensile strength of the material, as demonstrated in the Examples section of this specification. The enhancement of the physical properties of the material of the present invention and the degree of enhancement is dependent upon the operating parameters used. In view of the teachings of this specification, one of ordinary skill in the art will be able to discern the parameters appropriate to achieve a desired result without undue experimentation.

**[0228]** In one aspect, the ultrasonication of the aqueous suspension of the present invention comprises producing an sonicated suspension comprising microfibrillated cellulose with enhanced viscosity and/or tensile strength properties, the method comprising a step of microfibrillating a fibrous substrate comprising cellulose in an aqueous environment to produce an aqueous suspension comprising microfibrillated cellulose, and further comprising subjecting the aqueous suspension comprising microfibrillated cellulose to sonication to produce an aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties.

**[0229]** In one embodiment, a grinding media, as discussed above, is also used to produce the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties.

**[0230]** Ultrasonication of the aqueous suspension comprising microfibrillated cellulose is conducted with an ultrasonic probe or ultrasonic water bath, an ultrasonic homogenizer, an ultrasonic foil or an ultrasonic horn. The use of such devices is known to one of ordinary skill in

the art.

**[0231]** In an embodiment of the present invention, the methods of the present invention further comprises one or more of high shear mixing, homogenisation or refining either before or after the sonication step, all of which are known by one of ordinary skill in the art and is incorporated into the methods of the present invention without undue experimentation in view of the teachings of this specification.

**[0232]** In the invention, ultrasonication is advantageously used to re-disperse previously dewatered, dried or partially dried compositions of microfibrillated cellulose. The dried or partially dried compositions of microfibrillated is for example pelletized after dewatering and drying. Such dried or partially dried and optionally pelletized compositions of microfibrillated cellulose are re-suspended with the aid of ultrasonication devices of the types described in this specification.

**[0233]** In an embodiment ultrasonication is used as a post-treatment step on slurries of microfibrillated cellulose to improve one or more physical property of such slurries, for example, increased tensile strength and enhanced viscosity.

**[0234]** In an embodiment of the present invention, the tensile strength of the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties is increased by at least 5%, at least 10%, at least 20%, at least 50%, at least 100% or at least 200% over the aqueous suspension comprising microfibrillated cellulose not subject to sonication.

**[0235]** In an embodiment of the present invention, the viscosity of the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties is increased by at least 5%, at least by 10% or at least by 20%, by at least 50%, by at least 100% over the aqueous suspension comprising microfibrillated cellulose and inorganic particulate material not subject to sonication.

**[0236]** In the present invention, the aqueous suspension comprising microfibrillated cellulose is subject to sonication for at least 1 minute, at least 2 minutes, at least 5 minutes, at least 10 minutes and at least 20 minutes or longer. The length of time is determined by one of ordinary skill in the art based on the teachings of this specification.

**[0237]** In an embodiment of the present invention, the aqueous suspension comprising microfibrillated cellulose is subject to sonication at an energy compensation rate of up to 1000 kwh per tonne of dried fibrils, up to 2000 kwh per tonne, 2500 kwh per tonne of dried fibrils, up to 5000 kwh per tonne of dried fibrils and up to 10000 kwh per tonne of dried fibrils. As set forth in the Examples of this application, sonication was found to be more effective for re-dispersing and de-agglomerating microfibrillated cellulose or compositions of microfibrillated cellulose and inorganic particulate material that had been dewatered, dried and pelletized. In other embodiments, re-dispersion of slurries of slurries of microfibrillated cellulose or

compositions of microfibrillated cellulose and inorganic particulate material through sonication yielded improvements in product quality at energy inputs between 1000 and 2000 kWh/t.

**[0238]** In an embodiment, sonication of mineral free microfibrillated cellulose (e.g., birch) produced using the a pilot scale stirred media detritor (Supermill) yielded products with comparable specifications to microfibrillated cellulose made by grinding processes in, for example a Supermill, followed by a homogenization step when sonicated at about 1500 kWh/t.

**[0239]** In certain embodiments, the aqueous suspension comprising microfibrillated cellulose is sonicated by running the sonicator in continuous mode.

**[0240]** In preferred embodiments, the aqueous suspension comprising microfibrillated cellulose is formed into a semi-dry product prior to sonication. A belt pressed cake is one example of a semi-dried product suitable for use in the present invention. In certain embodiments, the belt press cake is further subjected to treatment in an air swept dryer and mill, such as an Attritor dryer. Often converting the product to a semi-dry product is done, for example, for ease of handling and/or transport. In the event of using a semi-dried product as a starting material, sonication not only provides enhanced physical properties to the material but also aids in disbursement of the material into solution in a process referred to as rewetting.

**[0241]** The sonication of the aqueous suspension comprising microfibrillated cellulose is not limited to any particular or specific sonication parameters as a change on one parameter compensates for a change in another parameter, within physical and practical limits of the equipment and material being sonicated. For example, lengthening sonication time compensates at least partly for using a reduced amplitude.

**[0242]** The embodiments, sonication is performed at an amplitude of up to 60%, up to 80%, up to 100% and up to 200% or more, to the physical limitations of the sonicator used. Said upper physical limits of amplitude of a particular device used are known to one of ordinary skill in the art.

**[0243]** The fibrous substrate comprising cellulose is in the form of a pulp, for example, a chemical pulp, or a chemithermomechanical pulp, or a mechanical pulp, or a recycled pulp, or a paper broke pulp, or a papermill waste stream, or waste from a papermill, or combinations thereof.

**[0244]** The grinding vessel is a tower mill or a stirred media detritor.

**[0245]** In an embodiment, the aqueous suspension comprising microfibrillated cellulose with enhanced viscosity and tensile strength properties obtained by the method of the present invention is suitable for use in a method of making paper or coating paper and is suitable for other use in other processes and materials where microfibrillated cellulose is typically used, examples of which are detailed below in the section entitled "Other Uses."

**Other Uses**

**[0246]** The compositions of microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material with enhanced viscosity and/or tensile strength properties and microfibrillated cellulose with enhanced viscosity and/or tensile strength are used in numerous applications. For example, the compositions of the present is used for paper, paper board and paper coatings, as discussed above; paints and other coatings as, for example a rheology modifier; inks; and as a thickener, stabilizer, and homogenizing agent for use in, for example, foods and food additives, pharmaceuticals, cosmetics, sunscreens, adhesives, sealants, consumer chemicals such as but not limited to detergents, fabric softeners and other household products; oilfield chemicals such as corrosion and scale inhibitors as well as an ingredient in petroleum by-products; and composites, such as wallboard and ceiling tiles. The compositions are also suitable for use in cement board, gypsum board/plasterboard; insulation core of structural insulated panels and fiber boards; fiberboards of all descriptions (including oriented particle board); cements and concretes; sound proofing; textured and masonry paints; antimicrobial and fire retardant wall boards; sealants and adhesives and caulks; insulation; partial or complete asbestos replacement; and foams, wherein the composition of the present invention, for example, provides strength, bulk and texture.

**Examples**

**[0247]** Embodiments of the present invention will now be described by way of illustration only, with reference to the following examples.

**[0248]** The following procedure we use to characterise the particle size distributions of mixtures of minerals (GCC or kaolin) and microfibrillated cellulose pulp fibres.

**- *calcium carbonate***

**[0249]** A sample of co-ground slurry sufficient to give 3 g dry material is weighed into a beaker, diluted to 60 g with deionised water, and mixed with 5 cm<sup>3</sup> of a solution of sodium polyacrylate of 1.5 w/v % active. Further deionised water is added with stirring to a final slurry weight of 80 g.

**- *kaolin***

**[0250]** A sample of co-ground slurry sufficient to give 5 g dry material is weighed into a beaker, diluted to 60g with deionised water, and mixed with 5 cm<sup>3</sup> of a solution of 1.0 wt% sodium

carbonate and 0.5 wt% sodium hexametaphosphate. Further deionized water is added with stirring to a final slurry weight of 80 g.

**[0251]** The slurry is then added in 1 cm<sup>3</sup> aliquots to water in the sample preparation unit attached to the Mastersizer S until the optimum level of obscuration is displayed (normally 10 - 15%). The light scattering analysis procedure is then carried out. The instrument range selected was 300RF : 0.05-900, and the beam length set to 2.4 mm. For co-ground samples containing calcium carbonate and fibre the refractive index for calcium carbonate (1.596) was used. For co-ground samples of kaolin and fibre the RI for kaolin (1.5295) was used.

**[0252]** The particle size distribution was calculated from Mie theory and gave the output as a differential volume based distribution. The presence of two distinct peaks was interpreted as arising from the mineral (finer peak) and fibre (coarser peak).

**[0253]** The finer mineral peak was fitted to the measured data points and subtracted mathematically from the distribution to leave the fibre peak, which was converted to a cumulative distribution. Similarly, the fibre peak was subtracted mathematically from the original distribution to leave the mineral peak, which was also converted to a cumulative distribution. Both these cumulative curves were then used to calculate the mean particle size ( $d_{50}$ ) and the steepness of the distribution ( $d_{30}/d_{70} \times 100$ ). The differential curve was used to find the modal particle size for both the mineral and fibre fractions.

**Examples 1-49 are not according to the invention.**

### **Example 1**

**[0254]** 400 cm<sup>3</sup> water and 750 g of marble flour (10wt% < 2µm particle size, by Sedigraph) were introduced into a grinding vessel and 1.5 kg of ceramic grinding media (Carbolite® 16/20, available from CARBO Ceramics Inc.) added. The mixture was stirred at 950 rpm for 60 minutes. The media was separated from the slurry and a small sample was removed to check the particle size (using a Micromeritics Sedigraph®) which was 57 wt% < 2µm.

**[0255]** The same grinder was used for each of the Examples. This grinder is a vertical mill comprising a cylindrical grinding vessel having an internal diameter of 14.5 cm and a vertical impeller shaft having a circular cross section and a diameter 1.8 cm. The shaft is equipped with 4 impellers positioned in an X design. The impellers have a circular cross section and a diameter 1.8 cm. The impellers are 6.5 cm long measured from the center of the vertical shaft to the impeller tip.

### **Example 2**

**[0256]** 400 cm<sup>3</sup> water and 750 g of marble flour (11-15 wt% < 2µm particle size, by Sedigraph) were introduced into a grinding vessel and 1.5 kg of ceramic grinding media (Carbolite® 16/20, available from CARBO Ceramics Inc.) added. The mixture was stirred at 950 rpm for 30 minutes. A small sample was removed and the particle size of the product was measured (using a Micromeritics Sedigraph®) at 57wt% < 2µm. An aliquot of bleached softwood pulp beaten in a Valley beater to a Canadian Standard Freeness (CSF) of 520 cm<sup>3</sup> was filtered through a screen in order to obtain a wet sheet at 20 wt% solids containing 37.5 dry g fibre. This sheet was added to the grinder and milling continued at 950 rpm for a further 30 minutes. 200 cm<sup>3</sup> of water was added during the grinding. The media was separated from the slurry, and the fibres greater than 38 µm removed using a BSS sieve having a mesh number of 400. The particle size of the filler composition was measured (using a Micromeritics Sedigraph®) and gave a result of 48 wt% < 2µm.

**Example 3**

**[0257]** The procedure described in Example 2 was repeated, this time continuing the second milling stage for 60 minutes. 200 cm<sup>3</sup> of water was added during the grinding. The particle size distribution of the product was measured and gave a value of 42 wt% < 2 µm.

**Example 4**

**[0258]** The procedure described in Example 2 was repeated, this time continuing the second milling stage for 120 minutes. 650 cm<sup>3</sup> of water was added during the grinding. The particle size distribution of the product was measured and gave a value of 40wt% < 2µm.

**Example 5**

**[0259]** The procedure described in Example 2 was repeated, this time continuing the second milling stage for 260 minutes. 1270 cm<sup>3</sup> of water was added during the grinding. The particle size distribution of the product was measured and gave a value of 40wt% < 2µm.

**Example 6**

**[0260]** The procedure described in Example 2 was repeated, this time continuing the second milling stage for 380 minutes. 1380 cm<sup>3</sup> of water was added during the grinding. The particle size distribution of the product was measured and gave a value of 57 wt% < 2 µm.

**Example 7 - evaluation of the products as fillers in paper**

**[0261]** Some of the products prepared according to the above examples were tested as fillers in paper handsheets. A batch of bleached chemical softwood pulp was used which was beaten in a Valley beater to give a CSF of 520 cm<sup>3</sup>. After disintegration and dilution to 2% thick stock, the fibre was diluted to 0.3 wt% consistency for sheet making.

**[0262]** Filler slurry was added together with retention aid (Ciba Percol 292, 0.02 wt% on furnish). Handsheets were made to a basis weight of 80 gm<sup>-2</sup> using a British handsheet mold according to standard methods, e.g., TAPPI T205 or SCAN C 26:76 (M 5:76).

**[0263]** The retention values of the fillers are listed below in Table 1, and show that the co-ground fillers have superior retention to the control filler.

**Table 1.** First pass retention values

| Ex. 1 control | Ex. 2 co-ground | Ex. 3 co-ground |
|---------------|-----------------|-----------------|
| 51%           | 63%             | 63%             |

**[0264]** Two separate sheet making studies were performed and the results are given in Tables 2 and 3 below. Paper properties are interpolated at 30wto/o loading and were measured according to standard test methods, e.g., TAPPI T220 or SCAN C28:76 (M 8:76).

- Burst strength: Messemmer Buchnel burst tester according to SCAN P 24.
- Tensile strength: Testometrics tensile tester according to SCAN P 16.
- Bendtsen porosity: Measured using a Bendtsen Model porosity tester in accordance with SCAN P21, SCAN P60, BS 4420 and Tappi UM 535.
- Bulk: This is the reciprocal of the apparent density as measured according to SCAN P7.
- ISO Brightness: The ISO brightness of handsheets was measured by means of an Elrepho Datacolour 3300 brightness meter fitted with a No. 8 filter (457nm wavelength), according to ISO 2470: 1999 E.
- Opacity: The opacity of a sample of paper is measured by means of an Elrepho Datacolor 3300 spectra-photometer using a wavelength appropriate to opacity measurement. The standard test method is ISO 2471. First, a measurement of the percentage of the incident light reflected is made with a stack of at least ten sheets of paper over a black cavity (Rinfinity). The stack of sheets is then replaced with a single sheet of paper, and a second measurement of the percentage reflectance of the single sheet on the black cover is made (R). The percentage opacity is then calculated from the formula: Percentage opacity = 100 x R/Rinfinity.

**Table 2**

| Filler   | Burst Index<br>Nm g <sup>-1</sup> <sub>1</sub> | Burst strength<br>%unfilled | Tensile index<br>Nm g <sup>-1</sup> | Tensile strength<br>%unfilled | Bendtsen porosity<br>cm <sup>3</sup> min <sup>-1</sup> | Bulk<br>cm <sup>3</sup><br>g <sup>-1</sup> | Brightness<br>F8 | % Opacity<br>F10 |
|----------|------------------------------------------------|-----------------------------|-------------------------------------|-------------------------------|--------------------------------------------------------|--------------------------------------------|------------------|------------------|
| Unfilled | 54                                             | 100                         | 59.5                                | 100                           | 790                                                    | 1.64                                       | 84.9             | 74.0             |
| Ex. 1    | 11                                             | 21.0                        | 14                                  | 26.0                          | 1900                                                   | 1.53                                       | 90.6             | 89.0             |
| Ex. 2    | 18                                             | 31.0                        | 24                                  | 40.5                          | 1490                                                   | 1.51                                       | 89.3             | 88.1             |
| Ex. 3    | 15                                             | 28.0                        | 23                                  | 39.0                          | 1490                                                   | 1.49                                       | 89.0             | 88.1             |

**Table 3**

| Filler   | Burst Index<br>Nm g <sup>-1</sup> <sub>1</sub> | Burst strength<br>%unfilled | Tensile index<br>Nm g <sup>-1</sup> | Tensile strength<br>%unfilled | Bendtsen porosity<br>cm <sup>3</sup> min <sup>-1</sup> | Bulk<br>cm <sup>3</sup><br>g <sup>-1</sup> | Brightness<br>F8 | % Opacity<br>F10 |
|----------|------------------------------------------------|-----------------------------|-------------------------------------|-------------------------------|--------------------------------------------------------|--------------------------------------------|------------------|------------------|
| Unfilled | 55.5                                           | 100                         | 63                                  | 100                           | 650                                                    | 1.59                                       | 85.5             | 73.7             |
| Ex. 1    | 9.5                                            | 17.5                        | 15                                  | 25.0                          | 2250                                                   | 1.55                                       | 90.7             | 88.9             |
| Ex.4     | 15                                             | 26.0                        | 22.5                                | 35.0                          | 700                                                    | 1.46                                       | 90.5             | 88.5             |
| Ex. 5    | 16                                             | 30.0                        | 23                                  | 35.0                          | 500                                                    | 1.44                                       | 90.1             | 88.9             |
| Ex.6     | 16                                             | 30.0                        | 24                                  | 39.0                          | 400                                                    | 1.45                                       | 89.7             | 89.4             |

**Example 8**

[0265] 4 dry kg of a kaolin filler, Intramax® 57, was dispersed in 6000 cm<sup>3</sup> water using a high energy mixer. The pH was 4.8. This was used as a stock suspension for further experiments. The particle size distribution was measured (using a Micromeritics Sedigraph®) and gave values of 57 wt% < 2 µm, and 38 wt% < 1 µm.

**Example 9**

[0266] 2 kg of the above stock suspension of kaolin was processed for 5 passes through a Manton Gaulin (APV) homogeniser at a pressure of 500 bar. The resulting product was used as a control in further papermaking tests. The particle size distribution was measured (using a Micromeritics Sedigraph®) and gave values of 62 wt% < 2 µm, and 43 wt% < 1 µm.

**Example 10**

[0267] A further 2 kg of the stock kaolin suspension was placed on a high energy mixer. A

suspension of bleached softwood pulp was beaten on a Valley beater to a CSF of 520 cm<sup>3</sup> and this was filtered on a standard consistency tester to give a wet sheet at 15% dry solids. 133.5 g of this wet pulp was added to the kaolin suspension and stirred until the fibres were well mixed with the kaolin, to give a level of 2.5 wt% dry pulp on dry kaolin. 440 cm<sup>3</sup> of water was also added to improve flowability. This suspension at 33 wt% solids was then passed through the Gaulin homogeniser under the same conditions as Example 9. The particle size distribution of the product was measured (using a Micromeritics Sedigraph®) and gave values of 62 wt% < 2 µm, and 45 wt% < 1 µm.

#### **Example 11**

[0268] The procedure described in Example 10 was repeated, this time adding 267 g wet pulp to 2 kg stock kaolin suspension, to give a level of 5 wt% dry pulp on dry kaolin. The suspension was also diluted to about 30 wt% solids with 440 cm<sup>3</sup> water, and the suspension processed through the homogeniser using the same conditions as Examples 9 and 10. The particle size distribution was measured (using a Micromeritics Sedigraph®) and gave values of 58.5 wt% < 2 µm, and 42 wt% < 1 µm.

#### **Example 12- evaluation of the products as fillers in paper**

[0269] The products prepared according to the above examples were tested as fillers in paper handsheets. A batch of bleached chemical softwood pulp was used which was beaten in a Valley beater to give a CSF of 520 cm<sup>3</sup>. After disintegration and dilution to 2% thick stock, the fibre was further diluted to 0.3 wt% consistency for sheet making. Filler slurry was added together with retention aid (Ciba Percol 292, 0.02 wt% on furnish). Handsheets were made to a basis weight of 80 gm<sup>-2</sup> using a British handsheet mold.

[0270] The retention values of the fillers are listed below in Table 4, and show that the co-processed fillers have superior retention to the control filler.

**Table 4.** First pass retention values

| Ex. 9 control | Ex. 10 co-processed | Ex. 11 co-processed |
|---------------|---------------------|---------------------|
| 54%           | 66%                 | 71%                 |

[0271] A sheet making study was performed and the results are given in Table 5 below. Paper properties are interpolated at 30 wt% loading.

**Table 5**

| Filler   | Tensile Index<br>Nmg <sup>-1</sup> | Tensile strength<br>%unfilled | Bendtsen porosity cm <sup>3</sup><br>min <sup>-1</sup> | Bulk cm <sup>3</sup><br>g <sup>-1</sup> | PPS Roughness<br>1000 kPa | Brightness F8 | % Opacity F10 |
|----------|------------------------------------|-------------------------------|--------------------------------------------------------|-----------------------------------------|---------------------------|---------------|---------------|
| Unfilled | 64                                 | 100                           | 785                                                    | 1.58                                    | 10.0                      | 85.5          | 72.8          |
| Ex. 9    | 20                                 | 31.0                          | 755                                                    | 1.48                                    | 8.4                       | 82.2          | 91.9          |
| Ex. 10   | 24                                 | 39.0                          | 610                                                    | 1.47                                    | 8.6                       | 82.2          | 91.9          |
| Ex. 11   | 30                                 | 46.0                          | 780                                                    | 1.50                                    | 9.0                       | 82.2          | 91.9          |

**Example 13**

[0272] 400 g of unrefined bleached softwood kraft pulp (Botnia Pine RM90) was soaked in 20 litres of water for 6 hours, then slushed in a mechanical mixer. The stock so obtained was then poured into a laboratory Valley beater and refined under load for 28 mins to obtain a sample of refined pulps beaten to 525 cm<sup>3</sup> Canadian standard Freeness (CSF). A second sample was prepared by slushing but not refining at all. The freeness results and refining times are given in Table 6 below:

**Table 6.** Refining Conditions

|               | Refining time, mins | CSF, cm <sup>2</sup> |
|---------------|---------------------|----------------------|
| Pulp Sample A | 0                   | 705                  |
| Sample B      | 28                  | 525                  |

[0273] Each of these pulps were then dewatered using a consistency tester (Testing Machines Inc.) to obtain a pad of wet pulp at between 13 and 18 wt% solids. This was then used in co-grinding experiments as detailed below:

630 g of a slurry of ground marble having a particle size (measured by Sedigraph) of 60 % < 2 µm e.s.d was weighed into a grinding vessel. The dry weight was 233 g. Wet pulp from the dewatering stage described above was added to give 11.6 g (dry weight) of pulp. The pulp was thoroughly mixed with the mineral slurry and then 1485 g Carbolite® 16/20 media and required water added to give a media volume, concentration (MVC) of 50% and a slurry solids content of 35 wt%. The samples were ground at 1000 RPM until an energy input of 2500 and 5000 kWh/t (expressed on dry fibre) had been imparted to the samples. The vessel was then removed from the grinder and the media separated using a screen having an aperture size of 600 µm.

[0274] Products made from Pulp sample A (unrefined) and B (refined to 525 cm<sup>3</sup>) were compared using the Filter Paper Burst Increase (FPBI) test (as described below). The results are summarised in Table 7.

**Table 7.** Filter paper burst increase

| Filler  | Pulp/ energy used during co-grinding | Wt% fibre on product by ash | Fibre d <sub>50</sub> µm | Fibre steepness(d <sub>30</sub> /d <sub>70</sub> x 100) | FPBI % |
|---------|--------------------------------------|-----------------------------|--------------------------|---------------------------------------------------------|--------|
| Control | Water only                           | -                           | -                        | -                                                       | 10.3   |
| 1       | Pulp A 2500 kWh/t                    | 4.3                         | 98.6                     | 28.7                                                    | 25.2   |
| 2       | Pulp A 5000 kWh/t                    | 4.9                         | 32.9                     | 37.7                                                    | 21.4   |
| 3       | Pulp B 2500 kWh/t                    | 5.0                         | 80.0                     | 31.7                                                    | 20.0   |
| 4       | Pulp B 5000 kWh/t                    | 5.0                         | 26.5                     | 40.2                                                    | 22.9   |

**- filter paper burst test**

[0275] This test was developed to predict the fibre reinforcing ability of a co-ground slurries containing MFC prepared in accordance with Example 13 above.

[0276] 15 cm diameter filter papers (No. 597, Schleicher & Schuell) were used. Sheets were selected by weight to be within 0.02 g of each other. A typical dry weight of a single sheet was 1.4 g.

[0277] A suspension of co-ground mineral and pulp was prepared as described above and diluted with water to a solids of 0.25%. A single filter paper selected above was wetted with water and placed on the wire of a standard consistency testing apparatus (TMI Testing Machines Inc., Ronkonkoma, NY). Aliquots of the suspension from 150 cm<sup>3</sup>, 200 cm<sup>3</sup>, 250 cm<sup>3</sup> and 300 cm<sup>3</sup> were carefully filtered using applied vacuum through the filter paper and the filtrates, if cloudy, re-passed through the mat to ensure good retention of the active components. The filter paper and its retained solids was then dried at 50% RH and 23°C supported on steel drying discs and separated by plastic drying rings (Testing Machines Inc.).

[0278] The dried papers were tested for burst strength using a Messemer Buchel automatic burst tester. 5 measurements were obtained on each sheet and averaged. The sheets were then dried at 100°C for 1 hour, placed in a sealed tared container, and weighed to 3 dp. A plot was constructed of sheet weight against burst pressure, from which the burst pressure at a weight of 2.0g was interpolated {a kPa}. The mean burst pressure of the filter paper itself {b kPa} was also measured on 3 selected sheets, conditioned under the same temperature and humidity. The increase in burst pressure was then calculated by the following equation :

**Filter paper burst increase (FPBI) = (a - b) / b x 100.**

[0279] As a control, water only was passed through the filter paper disc. This also had a

positive effect on burst, but significantly less than when MFC was present {see Table 7).

**[0280]** The samples produced above were additionally characterised in terms of their particle size using the Malvern Mastersizer {Malvern Instruments, UK}. The results are recorded in terms of the mean ( $d_{50}$ ) sizes of the pulp fractions. The particle size steepness of the fibre fraction was also recorded. These data are also listed in Table 7.

**[0281]** Samples made from Pulps A and B were further compared in a handsheet study. The host pulp for these fillers was prepared from the same Botnia RM90 batch beaten to a CSF of  $520 \text{ cm}^3$ , similar to Sample B. Retention aid was Percol 292 (Ciba) added at 0.06 wt% on total furnish solids. Handsheets were prepared at  $80 \text{ gm}^{-2}$  and tested for burst and tensile strength, bulk, Bendtsen porosity, reflectance at 457 nm (ISO brightness), and opacity. 3 loadings were obtained and results are interpolated to a loading level of 30 wt% (see Table 8). Filler designations refer to Table 7.

**[0282]** The results in Table 8 show that the co-ground fillers give increased strength, reduced porosity and increased opacity without detriment to the brightness, all desirable properties. The increase in strength is sufficient to allow the loading of filler to be increased from 25 wt% using standard GCC filler to 33 wt% with co-ground filler.

**Table 8.** Handsheet results

| Filler                               | Burst index<br>$\text{Nmg}^{-1}$ | Tensile<br>index $\text{Nmg}^{-1}$ | Bendsten<br>porosity $\text{cm}^3$<br>$\text{min}^{-1}$ | Bulk<br>$\text{cm}^3$<br>$\text{g}^{-1}$ | Brightness<br>F8 | %<br>Opacity<br>F10 |
|--------------------------------------|----------------------------------|------------------------------------|---------------------------------------------------------|------------------------------------------|------------------|---------------------|
| Unfilled                             | 65.4                             | 64.9                               | 481                                                     | 1.51                                     | 86.4             | 72.5                |
| Control<br>60-2 $\mu\text{m}$<br>GCC | 13.5                             | 19.5                               | 1500                                                    | 1.525                                    | 90.8             | 88.2                |
| 1                                    | 19.5                             | 25.5                               | 510                                                     | 1.43                                     | 91.0             | 89.1                |
| 2                                    | 19                               | 25                                 | 420                                                     | 1.40                                     | 90.9             | 89.1                |
| 3                                    | 18.5                             | 28.5                               | 340                                                     | 1.41                                     | 91.0             | 89.4                |
| 4                                    | 17.5                             | 25.5                               | 390                                                     | 1.41                                     | 91.0             | 89.9                |

#### **Example 14**

**[0283]** 400 g of unrefined bleached softwood kraft pulp (Botnia Pine RM90) was soaked in 20 litres of water for 6 hours, then slushed in a mechanical mixer. The stock so obtained was then poured into a laboratory Valley beater and refined under load for 28 mins to obtain a sample of refined pulp beaten to  $525 \text{ cm}^3$  Canadian Standard Freeness (CSF). The pulp was then dewatered using a consistency tester (Testing Machines Inc.) to obtain a pad of wet pulp at

19.1 wt% solids. This was then used in co-grinding experiments as detailed below:

**[0284]** 651 g of a slurry of Carbital 60HS™ (solids 77.9 wt%) was weighed into a grinding pot. 66.5 g of wet pulp was then added and mixed with the carbonate. 1485 g of Carbolite® 16/20 grinding media was then added followed by 147 g water to give a media volume concentration of 50%. The mixture was ground together at 1000 rpm until an energy input of 10,000 kWh/t (expressed on fibre) had been expended. The product was separated from the media using a 600 µm BSS screen. The solids content of the resulting slurry was 59.4 wt% and a Brookfield viscosity (100 rpm) of 10,000 mPa.s. The fibre content of the product was analysed by ashing at 450°C and the size of the mineral and pulp fractions measured using a Malvern Mastersizer.

#### **Example 15**

**[0285]** 352 g of a slurry of Carbital 60HS™ (solids 77.9 wt%) was weighed into a grinding pot. 71.8 g of wet pulp was then added and mixed with the carbonate. 1485 g of Carbolite 16/20 grinding media was then added followed by 296 g water to give a media volume concentration of 50%. The mixture was ground together at 1000 rpm until an energy input of 10,000 kWh/t (expressed on fibre) had been expended. The product was separated from the media using a 600 µm BSS screen. The solids content of the resulting slurry was 41.9 wt% and a Brookfield 100 rpm viscosity of 5000 mPa.s. The fibre content of the product was analysed by ashing at 450°C and the size of the mineral and pulp fractions measured using a Malvern Mastersizer.

#### **Example 16**

**[0286]** 287 g of a slurry of Carbital 60HS™ (solids 77.9 wt%) was weighed into a grinding pot. 87.9 g of wet pulp was then added and mixed with the carbonate. 1485 g of Carbolite 16/20 grinding media was then added followed by 311 g water to give a media volume concentration of 50%. The mixture was ground together at 1000 rpm until an energy input of 10,000 kWh/t (expressed on fibre) had been expended. The product was separated from the media using a 600 µm BSS screen. The solids content of the resulting slurry was 36.0 wt% and a Brookfield 100 rpm viscosity of 7000 mPa.s. The fibre content of the product was analysed by ashing at 450°C and the size of the mineral and pulp fractions measured using a Malvern Mastersizer.

**Table 9.** Physical properties of pigments

| Filler        | Mean GCC size, d <sub>50</sub> , µm | GCC steepness (d <sub>30</sub> /d <sub>70</sub> × 100) | Mean fibre size d <sub>50</sub> , µm | Wt % fibre in product |
|---------------|-------------------------------------|--------------------------------------------------------|--------------------------------------|-----------------------|
| Carbital 60HS | 1.49                                | 28.1                                                   | -                                    | 0                     |
| Carbital 90HS | 0.86                                | 35.6                                                   | -                                    | 0                     |
| Carbopaque 90 | 0.78                                | 40.6                                                   | -                                    | 0                     |

| Filler | Mean GCC size, $d_{50}$ , $\mu\text{m}$ | GCC steepness ( $d_{30}/d_{70} \times 100$ ) | Mean fibre size $d_{50}$ , $\mu\text{m}$ | Wt % fibre in product |
|--------|-----------------------------------------|----------------------------------------------|------------------------------------------|-----------------------|
| Ex 14  | 0.95                                    | 35.0                                         | 13.6                                     | 3.3                   |
| Ex 15  | 0.69                                    | 40.2                                         | 10.1                                     | 5.6                   |
| Ex 16  | 0.68                                    | 42.5                                         | 10.9                                     | 8.1                   |

[0287] Table 9 shows that, in addition to grinding the fibre to a fine particle size, the fineness and psd steepness of the GCC was also increased to match those of the finer control pigments, Carbital 90™ and Carbopaque 90™.

[0288] The references and co-ground pigments described above were made into coating colours and a coating study carried out according to the following examples.

**Example 17 (Control)**

[0289] 129 g of Carbital 60HS (=100g dry) were weighed into a beaker, mixed using a laboratory stirrer, and 14g of a 50% suspension of styrene - butadiene - acrylonitrile latex (DL920, Dow Chemical) added to give a binder dose of 7 parts latex per hundred of calcium carbonate (pph). 0.3 dry g of carboxymethyl cellulose (Finnfix 10, CP Kelco) was then added as a 12% solution, followed by 0.5 g of a solution of optical brightening agent (Blankophor P, Kemira). The pH was adjusted to 8.7 using NaOH. A second colour was prepared using an increased latex dose of 9 pph.

**Example 18 (Control)**

[0290] 129.7 g of Carbital 90HS (=100g dry) were weighed into a beaker, mixed using a laboratory stirrer, and 16g of a 50% suspension of styrene - butadiene - acrylonitrile latex (DL920, Dow Chemical) added to give a binder dose of 8 parts latex per hundred of calcium carbonate (pph). 0.3 dry g of carboxymethyl cellulose (Finnfix 10, CP Kelco) was then added as a 12% solution, followed by 0.5 g of a solution of optical brightening agent (Blankophor P, Kemira). The pH was adjusted to 8.9 using NaOH. A second colour was prepared using an increased latex dose of 10 pph.

**Example 19 (Control)**

[0291] 139 g of Carbopaque 90 (=100 g dry) were weighed into a beaker, mixed using a laboratory stirrer, and 16g of a 50% suspension of styrene - butadiene - acrylonitrile latex (DL920, Dow Chemical) added to give a binder dose of 8 parts latex per hundred of calcium

carbonate (pph). 0.3 dry g of carboxymethyl cellulose (Finnfix 10, CP Kelco) was then added as a 12% solution, followed by 0.5 g of a solution of optical brightening agent (Blankophor P, Kemira). The pH was adjusted to 8.6 using NaOH. A second colour was prepared using an increased latex dose of 10 pph.

**Example 20 (Control)**

**[0292]** 129.7 g of Carbital 90HS (=100g dry) were weighed into a beaker, and 2.5 g of a commercially available powdered cellulose of 1000 nm average particle size (manufacturer's value) intended for paper coating (Arbocel MF40, J.Rettenmaier & Sohne, Holzmuhle, Germany), was added with mixing using a laboratory stirrer. When the powder had been fully dispersed, 15g of a 50% suspension of styrene - butadiene - acrylonitrile latex (DL920, Dow Chemical) was added to give a binder dose of 7.5 parts latex per hundred of calcium carbonate (pph). 0.3 dry g of carboxymethyl cellulose (Finnfix 10, CP Kelco) was then added as a 12% solution, followed by 0.5 g of a solution of optical brightening agent (Blankophor P, Kemira). The pH was adjusted to 8.6 using NaOH.

**Example 21**

**[0293]** 173.4 g of the product prepared according to Ex 14 (=103 g dry) were weighed into a beaker, mixed using a laboratory stirrer, and 14 g of a 50% suspension of styrene - butadiene - acrylonitrile latex (DL920, Dow Chemical) added to give a binder dose of 7 parts latex per hundred of dry calcium carbonate (pph). 0.3 dry g of carboxymethyl cellulose (Finnfix 10, CP Kelco) was then added as a 10% solution, followed by 0.5 g of a solution of optical brightening agent (Blankophor P, Kemira). The pH was adjusted to 8.8 using NaOH. A second colour was prepared using an increased latex dose of 9 pph.

**Example 22**

**[0294]** 250.6 g of the product prepared according to Ex 15 (=105 g dry) were weighed into a beaker, mixed using a laboratory stirrer, and 14 g of a 50% suspension of styrene - butadiene - acrylonitrile latex (DL920, Dow Chemical) added to give a binder dose of 7 parts latex per hundred of dry calcium carbonate (pph). 0.3 dry g of carboxymethyl cellulose (Finnfix 10, CP Kelco) was then added as a 10% solution, followed by 0.375 g of a solution of optical brightening agent (Blankophor P, Kemira). The pH was adjusted to 8.6 using NaOH. A second colour was prepared using an increased latex dose of 9 pph.

**[0295]** The colours were coated onto a mechanical basepaper of substance 70 gm·2 using a laboratory web coater (Dow coater) with blade metering. The coat weight was adjusted by diluting the colour until the highest coat weight was obtained, subsequently increasing the

blade load to reduce the coat weight. Paper samples were produced having coat weight values from about 8 gm<sup>2</sup> to 12 gm<sup>2</sup>. The speed was about 10 m min<sup>-1</sup>.

**[0296]** The coated paper samples were then cut into strips and conditioned for 24 hours at 50% RH and 23°C before testing for brightness using a Datacolor Elrepho 3300 spectrophotometer. Reflectance measurements were made at 457 nm with and without the UV component in the incident light beam. The difference between the reflectance values with and without UV is recorded as the fluorescence. The smoothness of the coated papers was measured by an air leak method using a Parker Print Surf instrument at a pressure of 1000 kPa. Each of the values was plotted against the coat weight as measured by ash. The results were then interpolated to a common coat weight of 10 gm<sup>2</sup> and tabulated in Table 11.

**Table 10.** Coating colour properties

|       | Latex level pph | Solids wt% | Brookfield 100 rpm viscosity, mPa.s |
|-------|-----------------|------------|-------------------------------------|
| Ex 17 | 7               | 50.0       | 52                                  |
|       | 9               | 49.2       | 52                                  |
| Ex 18 | 8               | 50.0       | 62                                  |
|       | 10              | 42.7       | 86                                  |
| Ex 19 | 8               | 50.1       | 67                                  |
|       | 10              | 49.9       | 69                                  |
| Ex 20 | 7.5             | 45.8       | 67                                  |
| Ex 21 | 7               | 45.0       | 1008                                |
|       | 9               | 44.9       | 928                                 |
| Ex 22 | 7               | 38.2       | 1444                                |
|       | 9               | 38.3       | 1280                                |

**Table 11.** Paper properties at 10 gm<sup>2</sup>

|       | Latex level pph | Brightness +UV% | Fluorescence % | PPS Smoothness 1000kPa μm |
|-------|-----------------|-----------------|----------------|---------------------------|
| Ex 17 | 7               | 79.3            | 2.2            | 7.5                       |
|       | 9               | 79.5            | 2.3            | 7.6                       |
| Ex 18 | 8               | 79.5            | 2.4            | 7.8                       |
|       | 10              | 79.2            | 2.4            | 7.7                       |
| Ex 19 | 8               | 80.6            | 2.3            | 7.2                       |
|       | 10              | 80.5            | 2.2            | 7.2                       |
| Ex 20 | 7.5             | 80.4            | 3.1            | 7.6                       |
| Ex 21 | 7               | 83.0            | 4.9            | 6.7                       |
|       | 9               | 82.4            | 5.0            | 6.8                       |
| Ex 22 | 7               | 83.9            | 5.2            | 6.9                       |
|       | 9               | 83.7            | 5.2            | 6.9                       |

|  |                    |                    |                   |                                         |
|--|--------------------|--------------------|-------------------|-----------------------------------------|
|  | Latex level<br>pph | Brightness<br>+UV% | Fluorescence<br>% | PPS Smoothness<br>1000kPa $\mu\text{m}$ |
|--|--------------------|--------------------|-------------------|-----------------------------------------|

[0297] The results in Table 11 show that the invention gives increased brightness, fluorescence and increased smoothness.

#### **Example 23**

[0298] 630 g of a slurry of ground marble having a particle size (measured by Sedigraph) of  $60\% < 2 \mu\text{m}$  e.s.d was weighed into a grinding vessel. The dry weight was 233 g. 54 g of wet Eucalyptus pulp beaten to a CSF of  $525 \text{ cm}^3$  (see Table 12) were added, equivalent to 11.6 g dry weight. The pulp was thoroughly mixed with the mineral slurry and then 1485 g Carbolite 16/20 media and  $16 \text{ cm}^3$  water added. This equates to a media volume concentration (MVC) of 50% and a slurry solids content of 35 wt%. The samples were ground at 1000 RPM until an energy input of 2500 and 5000 kWh/t (expressed on dry fibre) had been imparted to the samples. The temperature reached  $55^\circ\text{C}$ . The vessel was then removed from the grinder and the media separated using a screen having an aperture size of  $600 \mu\text{m}$ .

#### **Example 24**

[0299] The procedure described in Example 23 was repeated, this time using a bleached kraft softwood pulp (Botnia Pine RM90) beaten to  $520 \text{ cm}^3$  CSF.

#### **Example 25**

[0300] The procedure described in Example 23 was repeated, this time using a sample of disintegrated thermomechanical pulp having a CSF of  $700 \text{ cm}^3$ .

#### **Example 26**

[0301] The procedure described in Example 23 was repeated, this time using a sample of Acacia pulp beaten to a CSF of  $520 \text{ cm}^3$ .

#### **Example 27**

**[0302]** The procedure described in Example 23 was repeated, this time using a sample of hardwood (birch) pulp beaten to a CSF of 520 cm<sup>3</sup>.

**[0303]** The fibre reinforcing ability of co-ground slurries containing MFC prepared in accordance with Examples 23-27 above was determined using the filter paper burst test described above. Results are given in table 12 below.

**[0304]** The samples produced above were additionally characterised in terms of their particle size using the Malvern Mastersizer (Malvern Instruments, UK). The results are recorded in terms of the mean ( $d_{50}$ ) sizes of the GCC and pulp fractions. The particle size steepness of the fibre fraction was also recorded. These data are also listed in Table 12. These results show that all the pulp types produce strength increases when subjected to co-grinding with GCC.

**Table 12.** Evaluation of the products using the filter paper test

| Example | Pulp                  | wt % fibre on mineral by ash | GCC $d_{50}$ $\mu\text{m}$ | Fibre $d_{50}$ $\mu\text{m}$ | Fibre steepness | FPBI % ( $d_{30}/d_{70} \times 100$ ) |
|---------|-----------------------|------------------------------|----------------------------|------------------------------|-----------------|---------------------------------------|
| Control | Water only            | -                            | -                          | -                            | -               | 10.3                                  |
| 23a     | Eucalyptus 2500 kWh/t | 4.6                          | 1.55                       | 54.0                         | 37.8            | 23.0                                  |
| 23b     | Eucalyptus 5000 kWh/t | 4.7                          | 1.3                        | 21.5                         | 40.0            | 22.2                                  |
| 24a     | TMP 2500 kWh/t        | 5.4                          | 1.55                       | 44.0                         | 32.8            | 17.0                                  |
| 24b     | TMP 5000 kWh/t        | 6.0                          | 1.4                        | 18.5                         | 38.1            | 26.4                                  |
| 25a     | Pine 2500 kWh/t       | 5.0                          | 1.6                        | 75.0                         | 33.2            | 20.0                                  |
| 25b     | Pine 5000 kWh/t       | 5.3                          | 1.4                        | 29.0                         | 37.3            | 21.3                                  |
| 26a     | Acacia 2500 kWh/t     | 5.3                          | 1.5                        | 54.5                         | 39.3            | 16.0                                  |
| 26b     | Acacia 5000 kWh/t     | 6.3                          | 1.3                        | 23.0                         | 40.1            | 21.8                                  |
| 27a     | Birch 2500 kWh/t      | 5.0                          | 1.55                       | 56.5                         | 36.0            | 21.0                                  |
| 27b     | Birch 5000 kWh/t      | 4.6                          | 1.15                       | 17.0                         | 37.8            | 25.5                                  |

### **Example 28**

**[0305]** 400 g of unrefined bleached softwood kraft pulp (Botnia Pine RM90) was soaked in 20 litres of water for 6 hours, then slushed in a mechanical mixer. The stock so obtained was then poured into a laboratory Valley beater and refined under load for 28 mins to obtain a sample of refined pulp beaten to 525 cm<sup>3</sup> Canadian Standard Freeness (CSF).

**[0306]** The pulp was then dewatered using a consistency tester (Testing Machines Inc.) to obtain a pad of wet pulp at 19.1 wt% solids. This was then used in grinding experiments as detailed below.

### **Example 29**

**[0307]** 584 g of a slurry of ground marble having a particle size (measured by Sedigraph) of 60% < 2 µm e.s.d was weighed into a grinding vessel. The dry weight was 231 g. Wet pulp from the dewatering stage described above (Example 28) was added to give 11.6 g (dry weight) of pulp. The pulp was thoroughly mixed with the mineral slurry and then 1485 g Carbolite 16/20 media and required water added to give a media volume concentration (MVC) of 50% and a slurry solids content of 35 wt%. The sample was ground at 1000 RPM until an energy input of 2500 kWh/t and 5000 kWh/t (expressed on dry fibre) had been imparted to the samples. The vessel was then removed from the grinder and the media separated using a screen having an aperture size of 600 µm. The fibre content of the product was analysed by ashing at 450°C and the size of the mineral and pulp fractions measured using a Malvern Mastersizer (see Table 13).

### **Example 30**

**[0308]** 176 g of a slurry of ground marble having a particle size (measured by Sedigraph) of 60% < 2 µm e.s.d was weighed into a grinding vessel. The dry weight was 65 g. Wet pulp from the dewatering stage described above was added to give 8.5 g (dry weight) of pulp. The pulp was thoroughly mixed with the mineral slurry and then 1485 g Carbolite 16/20 media and required water added to give a media volume concentration (MVC) of 50% and a slurry solids content of 12.5 wt%. The samples were ground at 1000 RPM until an energy input of 3750 and 5000 kWh/t (expressed on dry fibre) had been imparted to the samples. The vessel was then removed from the grinder and the media separated using a screen having an aperture size of 600 µm. The fibre content of the product was analysed by ashing at 450°C and the size of the mineral and pulp fractions measured using a Malvern Mastersizer (see Table 13).

**Table 13.**

| Filler              | GCC modal particle size, µm | Fibre d <sub>50</sub> , µm | wt % fibre in product |
|---------------------|-----------------------------|----------------------------|-----------------------|
| Control 60-2 µm GCC | 2.72                        | -                          | 0                     |
| Ex 29 2500 kW       | 2.1                         | 66.5                       | 4.5                   |

| Filler        | GCC modal particle size, $\mu\text{m}$ | Fibre $d_{50}$ , $\mu\text{m}$ | wt % fibre in product |
|---------------|----------------------------------------|--------------------------------|-----------------------|
| Ex 29 5000 kW | 1.73                                   | 26                             | 4.7                   |
| Ex 30 3750 kW | 1.61                                   | 65                             | 11.7                  |
| Ex 30 5000 kW | 1.41                                   | 42                             | 11.7                  |

**Example 31****- handsheet evaluation**

[0309] Samples made in Examples 29 and 30 were compared in a handsheet study. The control filler was the same 60% < 2 $\mu\text{m}$  ground marble used in the grinding experiments. The host pulp for these fillers was prepared from the same BotniaRM90 batch beaten to a CSF of 520  $\text{cm}^3$ . Retention aid was Percol 292 (Ciba) added at 0.06 wt% on total furnish solids. Handsheets were prepared at 80  $\text{gm}^{-2}$  and tested for burst and tensile strength, bulk, Bendtsen porosity, reflectance at 457 nm (ISO brightness), and opacity. Three loadings were obtained and results (Table 14) interpolated to a loading level of 30 wt%.

**Table 14.** Handsheet results

| Filler                         | Burst index $\text{Nm g}^{-1}$ | Tensile index $\text{Nm g}^{-1}$ | Bendsten porosity $\text{cm}^3 \text{min}^{-1}$ | Bulk $\text{cm}^3 \text{g}^{-1}$ | Brightness F8 | % Opacity F10 |
|--------------------------------|--------------------------------|----------------------------------|-------------------------------------------------|----------------------------------|---------------|---------------|
| Unfilled                       | 57.6                           | 59.8                             | 757                                             | 1.57                             | 86.8          | 74.1          |
| Control 60-2 $\mu\text{m}$ GCC | 13.0                           | 18.5                             | 1800                                            | 1.53                             | 91.6          | 88.0          |
| Ex 29 2500 kW                  | 18.0                           | 23.5                             | 500                                             | 1.45                             | 91.5          | 89.1          |
| Ex 29 5000 kW                  | 17.0                           | 21.5                             | 650                                             | 1.42                             | 91.4          | 89.1          |
| Ex 30 3750 kW                  | 24.0                           | 27.5                             | 130                                             | 1.40                             | 91.4          | 90.2          |
| Ex 30 5000 kW                  | 25.0                           | 27.5                             | 130                                             | 1.38                             | 91.3          | 90.2          |

[0310] The above results show that the co-ground fillers give increased strength, reduced porosity and increased opacity without detriment to the brightness, all desirable properties. Using fillers from Example 30 containing 11.7% co-ground fibre, the increase in strength is sufficient to allow the loading of filler to be increased from wt% using standard GCC filler to 40

wt% without loss of burst strength.

### **Example 32**

[0311] 321 g of a 72wt% slurry of filler kaolin (WP, Imerys) was weighed into a grinding pot. 105.9 g of wet unbleached North American kraft pine pulp at 10.9 wt% solids was then mixed in together with an additional 266 cm<sup>3</sup> water. 1485 g Carbolite 16/20 media was added and the mixture ground at 1000 rpm using a work input of 250 kWh/l expressed on dry mineral + pulp. The fibre content of the dry product after separation on a 700 µm screen was 3.9 wt% on the mineral measured by ignition at 950°C. The mean particle size (d<sub>50</sub>) of the fibre was estimated at 83 µm using a Malvern Mastersizer.

### **Example 33**

[0312] 206 g of a 72wt% slurry of filler kaolin (WP, Imerys) was weighed into a grinding pot. 108.7 g of wet unbleached North American kraft pine pulp at 10.9 wt% solids was then mixed in together with an additional 326 cm<sup>3</sup> water. 1485 g Carbolite 16/20 media was added and the mixture ground at 1000 rpm using a work input of 400 kWh/l expressed on mineral + pulp. The fibre content of the dry product after separation on a 700 µm screen was 6.2 wt%. The mean particle size (d<sub>50</sub>) of the fibre was estimated at 95 µm using a Malvern Mastersizer.

[0313] The host pulp for this study was the same batch of unbleached North American kraft pine pulp used in Examples 32 and 33. This was used as received from the manufacturer, diluting with water as required. Retention aid was Percol 292 (Ciba) added at 0.14 wt% on total furnish solids.

[0314] Handsheets were made at a target weight of 160 gm·2 with a target filler loading of 5 wt%. The sheets were pressed twice, and dried using a heated drum dryer, and conditioned for 12 hours at 50% RH and 23 C. A sample of the WP kaolin slurry was used as the control.

[0315] The sheets were tested for tensile strength, and clay content by ash. The results are set forth in Table 15 below:

**Table 15.** Linerboard results

| Filler     | Loading wt % | Tensile index (Nm g <sup>-1</sup> ) |
|------------|--------------|-------------------------------------|
| Unfilled   | 0            | 33.0                                |
| WP control | 4.4          | 23.1                                |
| Ex 32      | 3.9          | 31.1                                |
| Ex 33      | 3.7          | 29.4                                |

**[0316]** The above results show that the co-ground kaolin filler has considerably less weakening effect than unmodified kaolin in linerboard furnishes based on unbleached kraft pulp.

**Example 34**

**[0317]** 400 g of unrefined bleached softwood kraft pulp was soaked in 20 litres of water for 6 hours, then slushed in a mechanical mixer. The stock so obtained was then poured into a laboratory Valley beater and refined under load for 28 mins to obtain a sample of refined pulps beaten to 525 cm<sup>3</sup> Canadian Standard Freeness (CSF).

**[0318]** The pulp were then dewatered using a consistency tester (Testing Machines Inc.) to obtain a pad of wet pulp at between 13 and 18 wt% solids. This was then used in co-grinding experiments as detailed below:

**Example 35**

**[0319]** 750 g of dry English kaolin (Intramax 60) was made into a slurry by mixing with 540 cm<sup>3</sup> water and 1.9 g of a 40% solution of polyacrylate dispersant (Accumer 9300, Rohm & Haas). The pH was adjusted to 7 using NaOH, and the final solids was 57.2 wt%. The slurry was then transferred to a grinding pot and 37.5 dry g of the wet pulp prepared above (Example 34) mixed with it. The pH was adjusted to 9 with NaOH and 1500g of Carbolite 16/20 grinding media added. The mix was ground together for 60 minutes with addition of water as required to maintain fluidity. After 60 minutes the temperature reached 55°C. The ground product was then separated from the media using screen of 700µm aperture. The energy input was measured at 147 kWh/t, final solids was 45.8 wt%, pH 9.2, and the dry product had a fibre content of 4.95 wt% expressed on total product. The modal particle size of the fibre component was measured using a Malvern Mastersizer at 44 µm (e.s.d).

**Example 36**

**[0320]** 750 dry g of Intramax 60 was weighed into a grinding pot as a 57 wt% slurry as prepared above (Example 34). 37.5 dry g of the wet pulp was added and the pH was then adjusted to 4.0 using 10% orthophosphoric acid. 1500 g Carbolite 16/20 media was then added and the mix ground for 60 mins, after which time the temperature had reached 54°C. The work input was 140 kWh/t. The slurry was separated as before and the final solids was 42 wt%. The pH was 5.3. The fibre content of the product was measured at 4.0 wt%. Surprisingly, the modal particle size of the fibre component was measured using a Malvern Mastersizer at 0.50 µm (e.s.d), almost an order of magnitude finer than at pH 9. This unexpected observation suggests that grinding under acid conditions is much more effective than under alkaline

conditions.

### **Example 37**

**[0321]** 750 g dry marble flour was placed into a grinding pot with 400 cm<sup>3</sup> water and ground for 57 minutes with a work input of 120 kWh/t. The product was shown to have 58 wt% of particles <2µm esd, by Sedigraph. 37.5 dry g of wet pulp (as prepared in Example 34) was then mixed and the grind continued for a further 2 hours with the addition of 800 cm<sup>3</sup> further water and the expenditure of a further 313 kWh/t. The final temperature was 74°C, solids 37.4 wt%, and the fibre content of the dry product after separation on a 700 µm screen was 4.4 wt%. The modal particle size of the fibre was estimated at 50 µm using a Malvern Mastersizer.

### **Example 38**

**[0322]** 750 dry g of Optical HB (scalenohedral PCC) as a 34 % solids slurry was mixed with 37 g dry wt of wet pulp (as prepared in Example 34) and 200 cm<sup>3</sup> of water and 1500 g Carbolite 16/20 media added. The mixture was ground for 1 hour, using 154 kWh/t. The final temperature was 53°C and after separation of the media the slurry had a solids content of 41 wt% and the dried product had a fibre content of 5.3 wt%. The modal particle size of the fibre component was between 100 and 200 µm by Malvern Mastersizer.

### **Example 39**

#### ***- newsprint study***

**[0323]** These fillers were further compared in a handsheet study. The host pulp for these fillers was prepared by slushing a Northern European thermo-mechanical pulp sample. Since the pulp as received had a CSF of 50 cm<sup>3</sup>, no further refining was done. Retention aid was Percol 292 (Ciba) added at 0.02 wt% on total furnish solids. Handsheets were prepared at 50 gm-2 and tested for burst and tensile strength, bulk, Bendtsen porosity, reflectance at 457 nm (ISO brightness), and opacity. Three loadings were obtained and the results (see Table 16) are interpolated to a loading level of 10 wt%.

**[0324]** These results show that the co-ground fillers, especially with Intramax, give increased strength, and reduced porosity, all desirable properties, compared to the control fillers. Brightness and opacity are only slightly reduced. With Intramax, the increase in strength is sufficient to allow the loading of filler to be increased from 0 wt% to at least 8 wt% with co-ground filler without loss of strength. The filled paper would have lower porosity, and increased

brightness and opacity.

**Table 16.** Handsheet results: newsprint, 10 wt % filler loading

| Filler           | Burst index Nm g <sup>-1</sup> | Tensile index Nm g <sup>-1</sup> | Bendsten porosity cm <sup>3</sup> g <sup>-1</sup> | Bulk cm <sup>3</sup> g <sup>-1</sup> | Brightness F8 | % Opacity F10 |
|------------------|--------------------------------|----------------------------------|---------------------------------------------------|--------------------------------------|---------------|---------------|
| Unfilled         | 26.4                           | 41.6                             | 63                                                | 1.95                                 | 71.1          | 81.6          |
| Control Intramax | 20.5                           | 38.0                             | 60                                                | 1.87                                 | 72.7          | 85.7          |
| Ex 35            | 24.0                           | 41.0                             | 46                                                | 1.84                                 | 71.8          | 85.2          |
| Ex 36            | 24.5                           | 40.0                             | 46                                                | 1.85                                 | 71.5          | 85.4          |
| Control GCC      | 19.0                           | 32.0                             | 98                                                | 1.95                                 | 75.3          | 86.8          |
| Ex 37            | 20.0                           | 35.5                             | 88                                                | 1.93                                 | 74.8          | 86.5          |
| Control OCHB     | 19.9                           | 33.3                             | 153                                               | 2.00                                 | 75.7          | 87.6          |
| Ex 38            | 21.0                           | 35.5                             | 90                                                | 1.93                                 | 75.8          | 88.0          |

#### **Example 40**

#### ***- supercalendered magazine paper study***

[0325] A handsheet study was carried using the same pulp as in the newsprint study. The time sheets were made at 55 gm-2, with filler loadings covering the range from 30 to 40 wt%. Due to the higher loadings, the retention aid dose was increased to 0.07 wt% Percol 292. Handsheets were tested for burst and tensile strength, bulk, Bendtsen porosity, reflectance at 457 nm (ISO brightness), and opacity. Three loadings were obtained and the results (see Table 17) are interpolated to a loading level of 32 wt%.

**Table 17.** Handsheet results: SC magazine, 32 wt% filler loading

| Filler           | Burst index Nm g <sup>-1</sup> | Tensile index Nm g <sup>-1</sup> | Bendsten porosity cm <sup>3</sup> g <sup>-1</sup> | Bulk cm <sup>3</sup> g <sup>-1</sup> | Brightness F8 | % Opacity F10 |
|------------------|--------------------------------|----------------------------------|---------------------------------------------------|--------------------------------------|---------------|---------------|
| Unfilled         | 25.6                           | 45.2                             | 59                                                | 1.95                                 | 70.4          | 82.3          |
| Control Intramax | 11.0                           | 18.4                             | 71                                                | 1.66                                 | 76.2          | 91.4          |
| Ex 35            | 13.4                           | 22.0                             | 58                                                | 1.63                                 | 76.1          | 91.4          |
| Ex 36            | 12.2                           | 22.5                             | 57                                                | 1.61                                 | 75.9          | 91.4          |
| Control GCC      | 11.1                           | 17.2                             | 210                                               | 1.74                                 | 79.8          | 89.9          |

| Filler | Burst<br>index Nm<br>g <sup>-1</sup> | Tensile<br>index Nm g <sup>-1</sup> | Bendsten<br>porosity cm <sup>3</sup> g <sup>-1</sup> | Bulk<br>cm <sup>3</sup> g <sup>-1</sup> | Brightness<br>F8 | %<br>Opacity<br>F10 |
|--------|--------------------------------------|-------------------------------------|------------------------------------------------------|-----------------------------------------|------------------|---------------------|
| Ex 37  | 12.0                                 | 19.7                                | 150                                                  | 1.73                                    | 79.8             | 90.0                |

[0326] These results show that increased strength, reduced porosity, and similar brightness and opacity are obtained using co- ground fillers. In the case of Intramax, the loading could be increased from 30 wt% to at least 36 wt% without loss of strength, with reduced porosity and increased brightness and opacity.

Example 41

*- handsheet study*

[0327] The host pulp for this study was a batch of bleached chemical kraft softwood pulp which was slushed at 2% consistency and beaten in a Valley beater to a CSF of 520 cm<sup>3</sup>. Retention aid was Percol 292 (Ciba) added at 0.02 wt% on total furnish solids.

[0328] Two sets of sheets were made using scalenohedral precipitated calcium carbonate (Optical HB, Imerys) at 25 (Set A) and 32 wt% (Set B) loading levels. A further set of sheets (Set C) were made at a loading of 25 wt% Optical HB + 7 wt% of co-ground GCC from Example 37, so that the total loading was 32 wt%. A control set (Set D) was made at a loading 25 wt% Optical HB + 7 wt% of a standard GCC of 60% <2 um. A final set (Set E) was made using a 50/50 blend of Optical HB and co-ground GCC from Example 37 so that the total loading was 31 wt%.

[0329] Handsheets were prepared at 80 gm<sup>-2</sup>, pressed twice, and dried using a heated drum dryer, and conditioned for 12 hours at 50% RH and 23°C. The sheets were tested for tensile strength, bulk, Bendtsen porosity, reflectance at 457 nm (ISO brightness), and opacity. The results are set forth in the Table 18 below:

These results show that the co-ground GCC filler can be used to increase further the filler loading of PCC-filled sheets with lower loss in strength than if only PCC was used.

[0330] At the higher loadings, optical properties are maintained and porosity is reduced without serious loss of bulk.

Table 18. PCC top up results

| Filler                              | Tensile<br>index Nm g <sup>-1</sup> | Bendsten<br>porosity cm <sup>3</sup> g <sup>-1</sup> | Bulk<br>cm <sup>3</sup><br>g <sup>-1</sup> | Brightness<br>F8 | % Opacity F10<br>(80 gm <sup>-2</sup> ) |
|-------------------------------------|-------------------------------------|------------------------------------------------------|--------------------------------------------|------------------|-----------------------------------------|
| Unfilled                            | 66.6                                | 213                                                  | 1.50                                       | 84.0             | 73.8                                    |
| Set A 25.3%<br>Optical HB           | 29.4                                | 1131                                                 | 1.63                                       | 90.0             | 89.4                                    |
| Set B 31.7%<br>Optical HB           | 21.6                                | 1420                                                 | 1.62                                       | 90.8             | 90.7                                    |
| Set C 32.5%<br>OHB + Ex 37          | 25.0                                | 992                                                  | 1.57                                       | 90.8             | 90.8                                    |
| Set D 31.6%<br>OHB + Control<br>GCC | 24.0                                | 1123                                                 | 1.58                                       | 90.8             | 90.6                                    |
| Set E 30.9%<br>50/50 OCB/Ex<br>37   | 26.2                                | 824                                                  | 1.53                                       | 90.5             | 90.2                                    |

**Example 41**

**[0331]** Samples were prepared using a laboratory vertical stirred media mill equipped with a cylindrical, un-baffled grinding vessel of internal diameter - 14.5 cm. The mill was equipped with a vertical impeller having a circular cross section shaft of 1.8 cm diameter. The shaft was equipped with 4 impeller arms arranged in an X configuration at the bottom of the shaft. The impeller arms were of circular cross section and 1.8 cm diameter and were 6.5 cm long from shaft axis centreline to tip.

**[0332]** Grinding media (Carbolite, Carbo Ceramics Inc., USA) was of 16/20 mesh size and had specific gravity 2.7.

**[0333]** Ground Calcium Carbonate (GCC) (Intracarb 60, IMERYS Minerals, Belgium) had a sedigraph particle size of 60 % < 2 µm.

**[0334]** Pulp was bleached kraft softwood (Botnia Pine RM90) beaten to 520 cm<sup>3</sup> CSF.

**[0335]** Lab grinds were based on 1.5 kg of grinding media, 500/0 Media Volume Concentration (MVC), Pulp level of 5 wt.% of total solids, energy input 2500 kWM of pulp and impeller speed 1000 rpm. Grinds were performed in batch mode at a range of solids levels.

**[0336]** At the end of each grind the grinding chamber was removed from the mill and the contents removed. The grinding media was then separated from the product external to the mill.

**[0337]** The conditions for each grind and the resultant product properties are shown below in Table 19. The 8100 viscosity is the viscosity measured on a Brookfield viscometer (Brookfield Viscometers Ltd, Brookfield Technical Centre, Stadium Way, Harlow, Essex CM19 5GX, England) at 100 rpm.

**Table 19.**

| Sample | Grinding solids (wt.%) | B100 viscosity (mPas) | Pulp content (wt.%) | Fibre d <sub>50</sub> (µm) | Modal fibre particle size (µm) | Fibre steepness | Filter paper burst increase test (% increase in burst) |
|--------|------------------------|-----------------------|---------------------|----------------------------|--------------------------------|-----------------|--------------------------------------------------------|
| 1      | 35                     | 9600                  | 4.6                 | 87                         | 89                             | 30              | 20                                                     |
| 2      | 27.5                   | 4500                  | 4.6                 | -                          | 96                             | 28              | 17                                                     |
| 3      | 22.5                   | 1850                  | 4.3                 | 138                        | 259                            | 28              | 17                                                     |
| 4      | 17.5                   | 950                   | 4.1                 | 205                        | 352                            | 31              | 12                                                     |
| 5      | 12.5                   | 330                   | 3.6                 | 203                        | 409                            | 30              | 15                                                     |

**[0338]** These data indicate:

- The sample produced at the highest grinding solids has: the highest viscosity, the highest pulp content, the finest MFC size and the highest (best) filter paper burst increase test.
- Samples produced at lower grinding solids have lower viscosity, lower pulp content, coarser MFC size and lower filter paper burst increase tests.
- All of the samples have high viscosity compared to typical GCC products where B100 viscosities of < 200 mPas are typical.

#### **Example 42**

**[0339]** An attempt was made to produce a co-ground product in a full scale SMD equipped with a standard 250 µm screen ([www.metso.com](http://www.metso.com)). The grinding media, GCC and pulp were the same as in Example 41 except that the pulp was unrefined. The grinding media charge was 5 tonnes. The operating conditions were also similar to those used in Example 41; 50% MVC, pulp level of 5 wt. % of total solids, energy input 2500 kWh/t of pulp and a variety of impeller rpm to give a similar tip speed to that of the lab mill. The grinds were performed in continuous open circuit mode.

**[0340]** Initially, grinding was attempted at 35 wt.% total solids as in Example 41. However, it was not possible to produce any product under these conditions. The high viscosity product

would not flow through the screen and out of the mill. Instead the material built up in the mill. The grinding solids were lowered to less than 20 wt.% to obtain an acceptable flow through the mill and the products under these conditions did not show the same improvements in performance in paper as seen with the higher solids grinding.

**[0341]** For example, Sample 1 in Example 41 was produced in a lab batch grind (50% MVC, pulp level of 5% of total solids, energy input 2500 kWh/t of pulp and 1000 rpm impeller speed) at 35% solids. Samples 6 and 7 were produced in a full scale SMD equipped with a standard 250 µm screen under similar conditions except that the solids were lowered to <20% in order to achieve a flow through the mill.

**Table 20.**

| Sample ID    | Modal fibre particle size (um) | Filler loading for Burst Index of 20 Nm/g |
|--------------|--------------------------------|-------------------------------------------|
| 1            | 89                             | 28                                        |
| 6            | 194                            | 24                                        |
| 7            | 264                            | 23.5                                      |
| Lntracarb 60 | -                              | 20                                        |

**[0342]** These data show

- Both the lab and full scale produced MFC allowed increased filler loadings compared to the control.
- However, the MFC produced in the lab batch grind at 35% solids had finer fibre peak max and allowed a higher filler loading than the sample produced in an SMD where the solids had to be lowered to allow a flow through the mill
- NB It was not possible to operate the SMD under the high solids condition.

### **Example 43**

**[0343]** Samples were prepared using a pilot scale vertical stirred media mill equipped with a cylindrical, grinding vessel of internal diameter - 87 cm. The mill was equipped with a vertical impeller having a circular cross section shaft. The shaft was equipped with 4 impeller arms arranged in an X configuration at the bottom of the shaft. The impeller arms were of circular cross section and were 30 cm long from shaft axis centreline to tip.

**[0344]** The grinder was operated in batch mode. GCC and pulp were the same as in Example 41. Tests were performed at 50% MVC, and 39% solids with a pulp level of 5% of the total solids. The grinder rpm was 285. The pulp was unbeaten. Two sets of tests were performed. The first utilised 16/20 grinding media as in Example 41 and the second 3 mm media with the

same density. The fibre  $d_{50}$  and modal mineral particle size for both tests are shown in Table 21.

**Table 21.**

| Energy input (kWh/t) | Fibre $d_{50}$ ( $\mu\text{m}$ ) |      | Modal mineral particle size ( $\mu\text{m}$ ) |      |
|----------------------|----------------------------------|------|-----------------------------------------------|------|
|                      | 16/20                            | 3 mm | 16/20                                         | 3 mm |
| 3750                 | 73                               | 61   | 1.61                                          | 1.94 |
| 5000                 | 42                               | 44   | 1.42                                          | 1.83 |
| 7500                 | 15                               | 27   | 1.01                                          | 1.61 |
| 10000                | 8                                | 16   | 0.80                                          | 1.37 |

[0345] These data show that fibre grinding behavior was similar with coarser media especially at the lower energy inputs. However, mineral grinding was significantly reduced by use of the coarser media.

**Example 44**

[0346] These tests were performed in the same pilot grinder as was used in Example 43. GCC and pulp were the same as in Examples 41 and 42.

[0347] A sample was prepared in batch mode under the following conditions and with unbeaten pulp. Total solids 10%, pulp as percentage of total solids 20%; MVC 50%; 285 rpm; 3 mm media; Energy input 3500 kWh/t pulp. The resultant sample (sample 8) had a fibre  $d_{50}$  of 102  $\mu\text{m}$ .

[0348] In another test the same conditions were used but in this case the grinder was configured in recirculating batch mode with a 250  $\mu\text{m}$  screen. The flow rates were unacceptable because of the high viscosity of the product and no product was obtained.

[0349] In a further test a sample was prepared with the grinder configured in recirculating batch mode and a 1 mm screen was used and a high flow rate of 60 l/min was obtained. The resultant sample (sample 9) had a fibre  $d_{50}$  of 107  $\mu\text{m}$ .

[0350] The two samples were used in a handsheet evaluation using the same procedure as in Example 42. Results are summarized in Table 22.

**Table 22.**

| Sample ID | Configuration | Fibre $d_{50}$ ( $\mu\text{m}$ ) | Filler loading for 30% of unfilled burst |
|-----------|---------------|----------------------------------|------------------------------------------|
| 8         | Batch         | 102                              | 54                                       |
| 9         | Recirculating | 107                              | 50                                       |

| Sample ID    | Configuration | Fibre d <sub>50</sub> (µm) | Filler loading for 30% of unfilled burst |
|--------------|---------------|----------------------------|------------------------------------------|
|              | batch         |                            |                                          |
| Intracarb 60 | -             | -                          | 26                                       |

**[0351]** These data show that the use of coarse media and hence coarse screens allows the preparation of a co-ground product in a commercially viable, re-circulating batch (or continuous) configuration, despite the high viscosity of the product.

#### **Example 45**

**[0352]** Tests were performed in a pilot scale tower mill (Hosokawa Alpine model ANR 250). This is a vertical stirred media mill with an un-baffled cylindrical grinding chamber and a vertical impeller shaft equipped with a series of impeller rotor disks throughout its length. The mill is approximately two thirds filled with grinding media. In operation feed enters the mill at the bottom and passes through the grinding zone before rising to a quiescent zone where the grinding media starts to sediment away from the product. The product then exits the mill via a classifier wheel which serves to retain any further grinding media within the mill.

**[0353]** A co-ground product was prepared in an open circuit continuous configuration under the following conditions and with unbeaten pulp. Total solids 12.4 wt.%; pulp as percentage of total solids 20%; average MVC 22%; 500 rpm; 2-2.5 mm media of specific gravity about 6; Energy input 3200 kWh/t pulp. Flow rate into the mill 1.7 l/min

**[0354]** Initial attempts to run under these conditions were unsuccessful since the grinding media was carried over into the product. (An earlier attempt using 1 mm media failed as well also because of media carry over).

**[0355]** Subsequently a water addition of approx. 1 l/min was made immediately before the classifier wheel reducing the solids of the product exiting the mill to 8.1 wt%. Under these conditions all the media was retained in the mill.

**[0356]** The resultant sample (sample 10) had a fibre d<sub>50</sub> of 145 µm and a modal fibre particle size of 89 µm and was evaluated in a handsheet evaluation using the same procedure as in Example 42. Results are summarized in Table 23.

#### **Table 23.**

| Sample ID    | Configuration                                                           | Fibre d <sub>50</sub> (µm) | Modal Fibre particle size (µm) | Filler loading for 30% of unfilled burst |
|--------------|-------------------------------------------------------------------------|----------------------------|--------------------------------|------------------------------------------|
| 10           | Tower mill with coarse dense media and water addition before classifier | 145                        | 89                             | 49                                       |
| Intracarb 60 | -                                                                       | -                          |                                | 25                                       |

**[0357]** These data show that the use of coarse dense media and water addition immediately before the classifier wheel in a tower mill allows the preparation of co-ground in a, commercially viable configuration despite the high viscosity of the product.

#### **Example 46**

**[0358]** Samples are prepared using a laboratory vertical stirred media mill equipped with a cylindrical, un-baffled grinding vessel of internal diameter - 14.5 cm. The mill is equipped with a vertical impeller having a circular cross section shaft of 1.8 cm diameter. The shaft is equipped with 4 impeller arms arranged in an X configuration at the bottom of the shaft. The impeller arms are of circular cross section and 1.8 cm diameter and are 6.5 cm long from shaft axis centreline to tip.

**[0359]** Grinding media (Carbolite, Carbolite Ceramics Inc., USA) is 16/20 mesh size having a specific gravity of 2.7.

**[0360]** Pulp is bleached kraft softwood (Botnia Pine RM90) beaten to 520 cm<sup>3</sup> CSF.

**[0361]** Lab grinds are based on 1.5 kg of grinding media, 50% Media Volume Concentration (MVC) which may be varied, pulp levels cover the consistency range up to 10 wt.%, Energy inputs of up to 20 000 kWh/t of pulp are investigated using an impeller speed of 1000 rpm. Grinds are performed in batch mode at a range of solids levels.

**[0362]** At the end of each grind the grinding chamber would be removed from the mill and the contents removed. The grinding media is separated from the product external to the mill.

**[0363]** The MFC products are characterised for particle size using a Malvern light scattering device, for B100 viscosity using a Brookfield viscometer (Brookfield Viscometers Ltd, Brookfield Technical Centre, Stadium Way, Harlow, Essex CM19 5GX, England) at 100 rpm and the paper performance evaluated using the filter paper burst increase test and the handsheet method of Example 7 except that no filler is used or else the filler is Intracarb 60 (Imerys, Belgium).

**[0364]** The expectation is that the MFC produced gives increased filter paper burst tests and stronger hand sheets. It is envisaged that higher consistency and higher energy processing favour finer MFC and that there is an optimum MFC size for paper strength performance. The optimum performance will, likely, be obtained most efficiently by processing at high consistency.

**Example 47**

**[0365]** Samples are prepared using a pilot scale vertical stirred media mill equipped with a cylindrical, grinding vessel of internal diameter 87 cm. The mill is equipped with a vertical impeller having a circular cross section shaft. The shaft is equipped with 4 impeller arms arranged in an X configuration at the bottom of the shaft. The impeller arms are of circular cross section and are 30 cm long from shaft axis centreline to tip.

**[0366]** The grinder is operated in batch mode. Pulp is the same as in Example 46. Tests are performed under optimised conditions from Example 46. Grinder rpm is about 285. The pulp is unbeaten. Two sets of tests are performed. The first utilising 16/20 grinding media as in Example 46 and the second 3 mm media with the same density.

**[0367]** The MFC produced is characterised and evaluated using the method of Example 46.

**[0368]** It is envisaged that both grinding media would give similar psd MFC and that these MFC samples will allow production of handsheets with increased strength

**Example 48**

**[0369]** Tests are performed in the same pilot grinder as was used in Example 42. Pulp is the same as in Example 45. The grinding media is 3 mm.

**[0370]** A MFC sample is prepared in batch mode under the optimised conditions from Example 45. The MFC psd properties of the resultant sample will be determined.

**[0371]** In another test the same conditions would be used but in this case the grinder would be configured in recirculating batch mode with a 250 um screen. The flow rates would probably be unacceptable because of the high viscosity of the product and no product would be obtained.

**[0372]** In a further test a sample is prepared with the grinder configured in recirculating batch mode and a 1 mm screen is used and a high flow rate is expected.

**[0373]** The MFC produced is characterised and evaluated using the method of Example 45.

**[0374]** It is expected that the data will show that the use of coarse media and hence coarse screens allows the preparation of fine psd MFC at high consistency and low energy in a, commercially viable, re-circulating batch (or continuous), configuration despite the high viscosity of the product.

**Example 49**

**[0375]** Tests are performed in a pilot scale tower mill (Hosokawa Alpine model ANR 250). This is a vertical stirred media mill with an un-baffled cylindrical grinding chamber and a vertical impeller shaft equipped with a series of impeller rotor disks throughout its length. The mill is approximately two thirds filled with grinding media. In operation, feed enters the mill at the bottom and passes through the grinding zone before rising to a quiescent zone where the grinding media starts to sediment away from the product. The product then exits the mill via a classifier wheel which serves to retain any further grinding media within the mill.

**[0376]** A MFC sample is prepared in an open circuit continuous configuration under the optimised conditions from Example 46 and with unbeaten pulp. 2-2.5 mm grinding media of specific gravity about 6 is used. Energy inputs in the range 2000-15000 kWh/t pulp would be used.

**[0377]** It is expected that initial attempts to run under these conditions would be unsuccessful due to the grinding media being carried over into the product because of the high viscosity of the MFC.

**[0378]** Subsequently a water addition is made immediately before the classifier wheel reducing the solids of the product exiting the mill to a level where the media is not carried over. Under these conditions all the media is retained in the mill.

**[0379]** The MFC produced is characterised and evaluated using the method of Example 46.

**[0380]** The resultant sample will have a fine fibre psd. Evaluations in hand sheets will indicate that the MFC produced gave increases in burst strength of the sheets.

**[0381]** These data indicate that the use of coarse dense media and water addition immediately before the classifier wheel in a tower mill allows the preparation of MFC in a, commercially viable configuration despite the high viscosity of the product.

**Ultrasonic Treatment of MFC**

**Example 50**

**[0382]** The effect of an ultrasonic bath on various microfibrillated cellulose and microfibrillated cellulose and inorganic particulate material product forms.

**[0383]** The first study was to investigate the effect of using a laboratory Fisher brand FB11005 ultrasonic water bath on various microfibrillated cellulose and inorganic particulate material product forms. The microfibrillated cellulose and inorganic particulate material product form was a 50 POP (percentage of pulp) IC60/Botnia (*i.e.*, a 1:1 ratio) mixture of in the form of a slurry, belt pressed cake and a high solids dried 50 wt.% solids product. IC60 is a fine ground calcium carbonate available as Intracarb 60 from Imerys Minerals Limited. The samples were diluted to make a 20% POP (Percentage Of Pulp-- The POP or Percentage of Pulp is the percentage of the dry weight of the sample that is pulp or fibrils rather than inorganic particulate material) suspension at 6.25 wt.% solids. Each sample was subjected to various times within the ultrasonic bath and then subjected to 1 minute on the laboratory Silverson mixer at 7500 rpm; subsequent FLT (Nm/g: measurement of tensile strength) and viscosity measurements were made.

**[0384]** The FLT index is a tensile test developed to assess the quality of microfibrillated cellulose and re-dispersed microfibrillated cellulose. The POP of the test material is adjusted to 20% by adding whichever inorganic particulate was used in the production of the microfibrillated cellulose/ inorganic material composite (in the case of inorganic particulate free microfibrillated cellulose then 60wt.%<2um GCC calcium carbonate is used). A 220 gsm sheet is formed from this material using a bespoke Buchner filtration apparatus. The resultant sheet is conditioned and its tensile strength measured using an industry standard tensile tester.

**[0385]** Figure 2 shows the effect upon the viscosity of the microfibrillated cellulose and inorganic particulate material slurries. Within the first 5 minutes a small increase in the viscosity was observed. Tables 24 - 27 show strength properties of the microfibrillated cellulose and inorganic particulate material composition after ultrasonic bath treatment. The strength of the materials as measured by the FLT Index method have not changed significantly. The use of the ultrasonic bath for the re-dispersion of the microfibrillated cellulose and inorganic particulate material compositions for improvements in quality is not recommended. The low power input does not affect the strength properties but does influence the viscosity slightly.

**Table 24** - *Slurry properties*

| Sample                    | Time in US bath mins | Viscosity mPas | FLT Index Nm/g |
|---------------------------|----------------------|----------------|----------------|
| 50 POP IC60/Botnia slurry | 0                    | 1820           | 9.4            |
|                           | 1                    | 1940           | 8.7            |
|                           | 2                    | 1920           | 8.6            |
|                           | 3                    | 1920           | 8.7            |
|                           | 4                    | 1820           | 8.5            |
|                           | 5                    | 1820           | 8.8            |
|                           | 10                   | 1660           | 8.9            |

| Sample | Time in US bath<br>mins | Viscosity mPas | FLT Index Nm/g |
|--------|-------------------------|----------------|----------------|
|        | 20                      | 1520           | 9.0            |

**Table 25** - Belt pressed cake properties

| Sampl e                               | Time in US bath<br>mins | Viscosity<br>mPas | FLT Index<br>Nm/g |
|---------------------------------------|-------------------------|-------------------|-------------------|
| 50 POP IC60/Botnia belt press<br>cake | 0                       | 1240              | 7.7               |
|                                       | 1                       | 1280              | 8.2               |
|                                       | 2                       | 1360              | 8.2               |
|                                       | 3                       | 1360              | 8.1               |
|                                       | 4                       | 1360              | 8.5               |
|                                       | 5                       | 1300              | 8.0               |
|                                       | 10                      | 1320              | 7.4               |
|                                       | 20                      | 1340              | 7.5               |

**Table 26** - High solids dried 50 wt% properties

| Sample                                    | Time in US<br>bath | Viscosity<br>mPas | FLT Index<br>Nm/g |
|-------------------------------------------|--------------------|-------------------|-------------------|
| 50 POP IC60/Botnia product<br>@50% solids | 0                  | 1540              | 9.0               |
|                                           | 1                  | 1600              | 8.2               |
|                                           | 2                  | 1660              | 9.1               |
|                                           | 3                  | 1720              | 8.9               |
|                                           | 4                  | 1700              | 9.1               |
|                                           | 5                  | 1680              | 9.2               |
|                                           | 10                 | 1480              | 9.0               |
|                                           | 20                 | 1500              | 9.3               |

**Table 27** - High solids dried 60 wt% properties

| Sample                                     | Time in US<br>bath | Viscosity<br>mPas | FLT Index<br>Nm/g |
|--------------------------------------------|--------------------|-------------------|-------------------|
| 50 POP IC60/Botnia product @<br>60% solids | 0                  | 1100              | 6.8               |
|                                            | 1                  | 1220              | 7.3               |
|                                            | 2                  | 1020              | 7.2               |
|                                            | 3                  | 1100              | 6.7               |
|                                            | 4                  | 1100              | 5.8               |
|                                            | 5                  | 1180              | 6.7               |
|                                            | 10                 | 1120              | 7.0               |
|                                            | 20                 | 1100              | 6.9               |

**Example 51**

**[0386]** The effect of an ultrasonic probe on microfibrillated cellulose and inorganic particulate material slurry.

**[0387]** This experiment was to explore the effect that an ultrasonic probe has upon a microfibrillated cellulose and inorganic particulate material slurry. The ultrasonic probes used were "Sonics Vibracell VCX500 500 Watt model" with a "Probe horn CV33" and were used for the dispersion of mineral slurries prior to particle size measurement. The probe (horn) is specifically designed to operate at an amplitude of 40% but for this and further experiments it has been operated up to 100%.

**[0388]** The 50% POP IC60/Botnia (1:1 ratio) slurry at a total solids content of 1.7 wt.% was diluted to 20% POP with an IC60 ground calcium carbonate (70wt.% solids) slurry. This made the total solids of the samples 4.24 wt.%.

**[0389]** The ultrasonic probe was immersed into the slurry and was subjected to various times of ultrasound at various amplitudes. Figures 3 and 4 highlight the increase in FLT Index (Nm/g: measurement of tensile strength) and viscosity. It can be seen in the figures that the higher the amplitude the greater the increase in tensile strength. At 100% amplitude a 20% increase in FLT Index is achieved within 30 seconds compared to the original slurry. Compared to the original slurry a 33% increase within 2 minutes of applied ultrasound is achieved. At the reduced amplitude of 65%, the increase in FLT Index was 14% after 2 minutes of ultrasound compared to the feed slurry.

**Example 52**

**[0390]** The effect of pulsed ultrasound on microfibrillated cellulose and inorganic particulate material slurry.

**[0391]** The ultrasonic probe is operated in a continuous mode or pulsed mode. This experiment was to look at this effect. The microfibrillated cellulose and inorganic particulate material slurries were prepared as in Exp. 51, above and subjected to pulsed ultrasound. Figure 5 shows that an increase in FLT Index is made using the pulsed mode of operation. The use of the ultrasonic probe for the enhancement of the microfibrillated cellulose and inorganic particulate material improves product quality. The significant increase of the microfibrillated cellulose and inorganic particulate material slurry properties are achieved preferably using a high amplitude and run in a continuous mode.

**Example 53**

**[0392]** The effect of ceramic grinding media on ultrasound efficiency within a microfibrillated cellulose and inorganic particulate material slurry.

**[0393]** The production of a microfibrillated cellulose and inorganic particulate material product is achieved by the wet attrition milling of cellulose and mineral in the presence of a ceramic grinding media. This experiment was performed to investigate the effect of an ultrasonic process with some of ceramic grinding media present. Slurries of microfibrillated cellulose and inorganic particulate material as prepared in Examples 51 and 52, above were doped with 10 ceramic grinding media beads (~3 mm size). The materials were subjected to various energy inputs at 100% amplitude. Figure 6 shows that the presence of the media in the sample has no detrimental effect on the increase in FLT Index. The presence of the ceramic grinding media has no effect on the ultrasonic processing of the microfibrillated cellulose and inorganic particulate material slurry under these conditions.

**Example 54**

**[0394]** The effect of an ultrasonic probe microfibrillated cellulose and inorganic particulate material, 50% POP belt pressed cake.

**[0395]** A 50% POP IC60/Botnia belt press cake was the feed material for this study. The belt pressed cake was diluted to 20% POP, 6.25 wt.% solids using IC60 ground calcium carbonate slurry. Samples were made and subjected to:

1. i) 1 minute of high shear mixing on the Silverson mixer: The control
2. ii) Various times of ultrasound at 100% amplitude.

**[0396]** Figure 7 shows that the belt pressed cake is re-dispersed in water using the ultrasonic probe and the control FLT Index is achieved and surpassed.

**Example 55**

**[0397]** The effect of an ultrasonic probe on microfibrillated cellulose mineral free (no inorganic particulate material used in the fibrillation process) belt pressed cake.

**[0398]** To further explore the re-dispersion of a belt pressed cake, a mineral free version was evaluated. The belt pressed cake was diluted to 20% POP, 6.25 wt.% solids using IC60 ground calcium carbonate slurry. Samples were made and subjected to:

1. i) 1 minute of high shear mixing on the Silverson mixer: The control

2. ii) Various times of ultrasound at 100% amplitude.

**[0399]** Figure 8 highlights once again that ultrasonics alone achieves the sample properties that are produced with high shear mixing. High shear mixing combined with ultrasonics yields an improved tensile strength.

**Example 56**

**[0400]** The effect of an ultrasonic probe on 60wt.% a high solids dried microfibrillated cellulose and inorganic particulate material slurry.

**[0401]** A development product that is produced by drying a belt pressed cake was evaluated with the use of ultrasonics. This 50% POP IC60/Botnia 60 wt.% solids material requires 3 to 4 minutes of high shear Silverson mixing to achieve a FLT index of 9 Nm/g.

**[0402]** This study explored

1. i) The use of ultrasound as a pre cursor to high energy mixing
2. ii) The use of ultrasound as an additional aid to improve FLT values

**[0403]** Figure 9 shows that the effects of the ultrasonic energy is more effective utilised post high shear mixing. Figure 10 demonstrates the benefits of high shear mixing and ultrasonics combined. The use of ultrasonics is demonstrated to be an efficient way to re-disperse dried microfibrillated cellulose and inorganic particulate material product either with or without high shear mixing.

**[0404]** The results of Examples 50 - 56 show at least the following unexpected results of adding ultrasonic processing to microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material production:

- A microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material slurry's properties is substantially enhanced by ultrasonification if applied preferably by a probe or an ultrasonic water bath
- A higher amplitude yields a higher FLT Index
- Ceramic contaminants within a microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material slurry has no detrimental effect upon the ability of the ultrasound to affect the slurry's properties beneficially
- A microfibrillated cellulose or microfibrillated cellulose and inorganic particulate material belt press cake is very amenable to ultrasonics as a way to re-disperse it
- Ultrasonics can either replace high shear re-dispersion or enhance the procedure

- Higher solid content materials can be re-dispersed using ultrasonics.

### **Example 57**

**[0405]** The following trials were carried out to evaluate the properties of microfibrillated cellulose and inorganic particulate material that had been fibrillated and then dewatered, dried and pelletized to produce an approximate 50% solids concentration. The dried microfibrillated cellulose and inorganic particulate material composition was then made down to various fiber slurry concentrations between 0.7% and 3.4%. The fibrillated cellulose and inorganic particulate material (mineral) product was a 50% percentage of pulp (POP) aqueous composition produced by fibrillating a mixture of 50% POP Botnia pulp/ground calcium carbonate IC60 (*i.e.*, a 1:1 wt. ratio) in the form of a slurry. The overall solids of the pelletized product used was 50 wt.%. The operating pressure for the sonication trials was varied from 0 to 4 bar pressure to determine the optimum pressure for sonication. The trials were carried out at different temperatures (20° C to 50 °C) to determine the optimal process temperature. Cooling water at various flow rates was pumped into a flow cell cooling jacket and used to maintain the operating temperature at the required level.

**[0406]** The microfibrillated cellulose and inorganic particulate materials slurry was subjected to grinding in a stirred media detritor. The slurry was screened using two screening stages through slotted screens of 250 microns and 120 microns, respectively. The microfibrillated cellulose and inorganic particulate material slurry was dewatered using a belt press followed by further drying in an air swept Atritor dryer & mill (available from Atritor Limited, 12 The Stampings, Blue Ribbon Park, Coventry, West Midlands, England). An Atritor mill is an air-swept mill or dryer having the capability to introduce a stream of hot air for drying and milling materials, in order to process and dry the microfibrillated cellulose and inorganic particulate material (*e.g.*, calcium carbonate) composition utilized in the trials. Other equivalent air swept dryer and mills are known to one of ordinary skill in the art.

**[0407]** The feed solids to the belt press was 2 wt.% of the 50 wt.% POP slurry. The feed solids to the Atritor dryer and mill was 30 wt.% at a bulk density of 0.5 kg/L. The inlet temperature of the Atritor mill was set at 150-170°C. and the outlet temperature of air was measured as 68-75° C. Product solids content of the dried microfibrillated and inorganic particulate material product was 50 wt.%. The dried material was thereafter fed into a Kahl pellet mill with an inlet and outlet temperature of 16° and thereby pelletized.

**[0408]** The ultrasonic unit used in the trials was a Hielscher UIP1000hd industrial scale ultrasonic processor available from Hielscher Ultrasonics GmbH (Oderstr. 53 D-14513 Teltow, Germany and 530 Ringwood Ave. Lembo & Gray Bldg. Wanaque, NJ 07465, USA).

**[0409]** The test material was recirculated from a feed tank to the ultrasonic flow cell. The

volume in the feed tank was 2.5L. The flow rate during all trials was maintained at approximately 1.5 L/min.. A progressive cavity pump was used for pumping. 250 ml samples were taken after 0, 1, 2, 4 and 10 minutes.

**[0410]** All samples collected from trials, which used made-down pelletized microfibrillated cellulose and inorganic particulate material as feed, were assessed for nibs using the TAPPI dirt count method. Nibs are agglomerates in the microfibrillated cellulose and inorganic particulate material tensile (FLT) sheet that would not have been broken down or de-agglomerated after processing.

**[0411]** Based on the recommendations from the ultrasonic supplier, all the trials were conducted using the largest booster (B4-2.2) and BS4d22 sonotrode.

**[0412]** Once the optimum pressure and temperature were identified, trials at different fiber solids, i.e. 0.7%, 1.5%, 2.5% and 3.3% were carried out. Thus, the optimum fiber solids for sonication were identified.

***Example 58: Optimization trials - effect of pressure.***

**[0413]** These trials were conducted using handmade-down pellets (low energy). The pellets were made using microfibrillated cellulose and inorganic particulate material dried in an air swept Attritor dryer and mill. The microfibrillated cellulose and inorganic particulate material was tested at 50% solids and 50% POP (Botnia pulp / ground calcium carbonate IC60). The objective was to re-disperse and de-agglomerate pelletized microfibrillated cellulose and inorganic particulate material (except where otherwise indicated) using sonication and to recover the product quality in terms of FLT index and nibs of the initial slurry product before being dewatered, dried and pelletized. The made down pellets were diluted to 6.6% total solids (3.3% fiber solids) and sonication trials were carried out in recirculation mode at the different pressures (0 to 4 bar). Results from these trials are presented in Figures 11A to C.

**[0414]** Overall FLT index did not show a significant difference when processing at higher pressures; but from a scaling point of view, it was important to ensure that the ultrasonic unit was drawing as much power as possible during the processing of microfibrillated cellulose and inorganic particulate material. The average power draw vs. processing time chart shows that the optimum pressure was 3 bar.

***Example 59: Optimization trials - effect of temperature.***

**[0415]** These trials were conducted using handmade-down pellets (low energy input). The made down pellets were diluted to 6.6% total solids (3.3% fiber solids) and sonication trials were carried out in recirculation mode at the different temperatures (20° C to 50° C).

Processing temperature was controlled by adjusting the flow rate of the cooling water in the flow cell water jacket. Results from these trials are shown in Figures 12 A to C.

**[0416]** FLT index showed no significant difference at the different temperatures assessed. Operating at lower temperatures results in higher power draw from the ultrasonic unit, which is preferable. Therefore, it was demonstrated that 20 °C is an optimal temperature when sonicating microfibrillated cellulose.

**[0417]** *Example 60:* Trials using product that has been made down using a laboratory high shear mixer.

**[0418]** Pelletized microfibrillated cellulose and inorganic particulate material, as described in Example 57, was made down using a laboratory Silverson high shear mixer. About 200 kWh/t of energy was used during the make down. Trials were carried out in recirculation mode. Unlike in previous trials the high shear product was not recirculated for 30 min before sonication trials began. The high shear product was sonicated at different fiber solids, see Figures 13A and B.

**[0419]** Similar to trials reported earlier, the optimum energy was about 2000 kWh/t. As depicted in Figures 13 A and B, sonicating at lower solids (0.7% and 1.5%) gave the best products in terms of FLT index and viscosity.

**[0420]** *Example 61:* Post treatment trials using continuous ground microfibrillated cellulose and inorganic particulate material slurry.

**[0421]** Microfibrillated cellulose and inorganic particulate material slurry was obtained pressure screening (i.e., never dewatered or dried product). Trials were carried out to determine the effectiveness of sonication in post treating microfibrillated cellulose and inorganic particulate material slurry after the grinding process. Data on the trials is presented in Figures 14 A to C.

**[0422]** There was an increase in FLT and viscosity in these trials, which is an indication of improved product quality. Processing at lower solids gives better products at a given energy input. The energy required to give acceptable product improvement is high, i.e., more than 1000 kWh/t, which makes ultrasonic technology more energy intensive in post treating microfibrillated cellulose and inorganic particulate material slurry, though product performance is enhanced.

**Example 62: Post treatment trials using refiner product.**

**[0423]** Pelletized microfibrillated cellulose and inorganic particulate material, prepared in accordance with the procedures of Example 57, was made down using a pilot pulper and subsequently refined using a pilot refiner. The product from the refiner was collected and trials were carried out to investigate the effect of sonication. Trials were done at 3 solids levels -

1.5%, 2.5% and 3.3% fiber solids. The data is reported in Figures 15 A to C. Improvement in product quality was shown by the increase in FLT index and viscosity. The energy required to increase the FLT by 1.0 was about 2000 kWh/t. Post treatment of refiner product using sonication was very energy intensive.

**[0424]** *Example 63:* Post treatment of mineral free microfibrillated cellulose and mineral free microfibrillated cellulose subjected to an additional pass through a homogenizer as well as an ultrasonic treatment step.

**[0425]** Mineral free (100% POP/ Birch pulp microfibrillated cellulose was produced in a pilot stirred media detritor (Supermill) grinder using high density zirconia media (specific gravity of 6). The mineral free product, composed of mostly cellulose (organic matter) was passed through a pilot homogenizer to produce a more finely fibrillated, mineral free, microfibrillated cellulose. Trials were then carried out to determine the effect of sonication on mineral free microfibrillated ground product with and without a homogenization step. The data on these trials is reported in Figures 16A and B.

**[0426]** The data in Figures 16A and B indicate that it is possible to produce microfibrillated cellulose from mineral free grinder product (birch) using sonication and without a homogenization step. The FLT of microfibrillated cellulose subjected to a homogenization step is greater than 15 Nm/g. The trials reported in Figures 16A and B after sonicating the mineral free ground product up to about 1500 kWh/t produced a ground microfibrillated cellulose with FLT indices and  $d_{50}$  particle sizes in the range of ground microfibrillated cellulose subjected to a homogenization step.

**[0427]** The Examples set forth above are illustrative of the many embodiments of the invention disclosed herein by the inventors and are not intended to be limitations of the invention.

## REFERENCES CITED IN THE DESCRIPTION

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### Patent documents cited in the description

- [JPS58206601A \[0008\]](#)
- [US20150225550A \[0009\]](#)
- [US20100279019A \[0010\]](#)

- EP614948A [0034]
- US5576617A [0089]

**Non-patent literature cited in the description**

- Paper Coating PigmentsTAPPI Monograph Serie, 34-35 [0033]
- CHEMICAL ABSTRACTS, 90045-36-6 [0183]
- CHEMICAL ABSTRACTS, 55956-84-9 [0183]
- CHEMICAL ABSTRACTS, 2634-33-5 [0183]
- Pulp and Paper International, 1994, 18- [0187]

**Patentkrav**

1. Fremgangsmåde til redispergering af afvandet, delvist tørret eller i det væsentlige tørret mikrofibrilleret cellulose, hvilken fremgangsmåde omfatter trinnene:

- 5 (a) tilsætning af en mængde egnet dispergerende væske til en tank, som har mindst et første og et andet indløb og et udløb, hvor tanken endvidere omfatter en blander og en pumpe, som er fastgjort til udløbet;
- 10 (b) tilsætning af en mængde afvandet, delvist tørret eller i det væsentlige tørret mikrofibrilleret cellulose til tanken gennem det første indløb i tilstrækkelig mængde til at frembringe en flydende sammensætning af mikrofibrilleret cellulose ved en ønsket faststofkoncentration på 0,5 til 5% fiberfaststoffer;
- 15 (c) blanding af den dispergerende væske og den afvandede, delvist tørrede eller i det væsentlige tørrede mikrofibrillerede cellulose i tanken med blanderen for delvis at agglomerere og redispergere den mikrofibrillerede cellulose til dannelse af en flydende opslæmning;
- 20 (d) pumpning af den flydende opslæmning med pumpen til et indløb på en strømningscelle, hvor strømningscellen omfatter en eller flere ultralydssonder i serie og mindst et første og et andet udløb, hvor det andet udløb på strømningscellen er forbundet med det andet indløb på tanken, hvorved der tilvejebringes en kontinuerlig recirkulationssløjfe, der sørger for kontinuerlig tilførsel af ultralydsenergi til opslæmningen i en ønsket tidsperiode og/eller samlet energitilførselsområde, hvor strømningscellen omfatter en justerbar ventil ved det andet udløb for at generere modtryk for den recirkulerede opslæmning på fra 0 til 4 bar, hvor endvidere
- 25 væskesammensætningen, der omfatter mikrofibrilleret cellulose fra trin (c), kontinuerligt recirkuleres gennem recirkulationssløjfen ved en temperatur på 20°C til 50°C;
- 30 (e) kontinuerlig anvendelse af en ultralydsenergitilførsel til opslæmningen på 200 til 10.000 kWh/t via ultralydssonden ved et frekvensområde fra 19 til 100 kHz og ved en amplitude på op til 60%, op til 100% eller op til 200% til fysiske begrænsninger af den ultralydsanordning, der bruges i 1 til 120 minutter;

- (f) samling af den redispergerede suspension, der omfatter mikrofibrilleret cellulose med forbedret trækstyrke og/eller viskositetsegenskaber fra det første udløb på strømningscellen til en egnet opbevaringsbeholder.

- 5     **2.** Fremgangsmåde ifølge krav 1, hvor den afvandede, delvist tørrede eller i det væsentlige tørrede mikrofibrillerede cellulosesammensætning endvidere omfatter mindst ét uorganisk partikelformigt materiale.
- 10     **3.** Fremgangsmåde ifølge krav 1 eller 2, hvor den dispergerede væske er vand.
- 4.** Fremgangsmåde ifølge krav 1 eller 2, hvor ultralydsenergitilførslen er fra ca. 1000 kWh/t til ca. 2000 kWh/t, eller hvor ultralydsenergitilførslen er fra ca. 200 kWh/t til ca. 400 kWh/t.
- 15     **5.** Fremgangsmåde ifølge krav 1 eller 2, hvor strømningscellen har en kølekappe til opretholdelse af en temperatur af suspensionen af mikrofibrilleret cellulose i området fra ca. 20°C til ca. 50°C, som f.eks. stuetemperatur eller 20°C.
- 20     **6.** Fremgangsmåde ifølge krav 1, hvor bagtrykket af den recirkulerede væske er 3 bar.
- 7.** Fremgangsmåde ifølge krav 1 eller 2, hvor strømningscellen endvidere omfatter en eller flere boostere for mekanisk at forøge eller formindske amplituden af den mindst ene ultralydssonde.
- 25     **8.** Fremgangsmåde ifølge krav 1 eller 2, hvor væskesammensætningen af den mikrofibrillerede cellulose har ca. 0,5% til ca. 1 % fiberfaststoffer.
- 30     **9.** Fremgangsmåde ifølge krav 1 eller 2, hvor væskesammensætningen af den mikrofibrillerede cellulose har ca. 1,5% fiberfaststoffer.

10. Fremgangsmåde ifølge krav 1 eller 2, hvor væskesammensætningen af den mikrofibrillerede cellulose har ca. 1,8% fiberfaststoffer.
- 5 11. Fremgangsmåde ifølge krav 1 eller 2, hvor væskesammensætningen af den mikrofibrillerede cellulose har ca. 2,5% fiberfaststoffer.
12. Fremgangsmåde ifølge krav 1 eller 2, hvor den mikrofibrillerede cellulose eller den mikrofibrillerede cellulosesammensætning, der omfatter uorganisk partikelformet materiale, pelleteres.
- 10 13. Fremgangsmåde ifølge krav 1, hvor ultralydsenergien anvendes i ca. 30 minutter.
14. Fremgangsmåde ifølge krav 1 eller 2, hvor ultralydsenergien anvendes, indtil der er opnået en specificeret ultralydsenergitilførsel på mere end 200 kWh/t, som
- 15 f.eks. mere end 400 kWh/t.
15. Fremgangsmåde ifølge krav 2, hvor ultralydsenergien anvendes, indtil der er opnået en specificeret kumulativ energitilførsel som f.eks. 500 kWh/t eller 1000 kWh/t eller 1500 kWh/t eller 2000 kWh/t eller 2500 kWh/t.
- 20 16. Fremgangsmåde ifølge krav 1 eller 2, hvor recirkulationssløjfen endvidere omfatter en højforskydningsblander.
17. Fremgangsmåde ifølge krav 1 eller 2, hvor den flydende sammensætning, der
- 25 omfatter mikrofibrilleringscellulose, recirkuleres i ca. 30 til ca. 120 minutter som f.eks. i ca. 30 minutter.
18. Fremgangsmåde ifølge krav 1 eller 2, hvor ultralydsbehandling køres i pulsmodus.
- 30 19. Fremgangsmåde ifølge krav 1 eller 2, hvor det delvist tørre produkt formes til en båndpresset kage inden ultralydsbehandling.

- 5      **20.** Fremgangsmåde ifølge krav 1 eller 2, hvor den mikrofibrillerede cellulose kan fremstilles af kemisk papirmasse eller en kemitermomekanisk papirmasse eller en mekanisk papirmasse eller en genbrugspapirmasse eller en frasorteret papirmasse eller en papirmølleaffaldsstrøm eller affald fra en papirmølle eller kombinationer deraf.
- 10      **21.** Fremgangsmåde ifølge krav 2, hvor det uorganiske partikelformige materiale er et jordalkalimetalscarbonat eller -sulfat som f.eks. calciumcarbonat, magnesiumcarbonat, dolomit, gips, en vandig kandslitler såsom kaolin, halloysit- eller keramikler, en vandfri (calcineret) kandslitler såsom metakaolin eller fuldt calcineret kaolin, talkum, glimmer, perlit eller diatoméjerd, eller kombinationer deraf, og mere foretrukket calciumcarbonat eller kaolin.
- 15      **22.** Fremgangsmåde ifølge krav 1 eller 2, hvor den vandige suspension, som omfatter mikrofibrilleret cellulose og uorganisk partikelformet materiale med forbedret viskositet og trækstyrkeegenskaber opnået via fremgangsmåden, er egnet til anvendelse i en fremgangsmåde til fremstilling af papir eller belægningspapir, malinger og belægninger, trykfarver, oliefeltkemikalier, kompositter, forbrugerprodukter, kosmetiske produkter, farmakologiske produkter og fødevarerprodukter.
- 20      **23.** Fremgangsmåde ifølge krav 1, hvor fremgangsmåden endvidere omfatter en eller flere blandinger med høj forskydningskraft, homogenisering og raffinering enten før eller efter ultralydsbehandlingstrinnet.

# DRAWINGS



Figure 1

50 POP IC60/Botnia: Effect of ultrasonic bath pre treatment

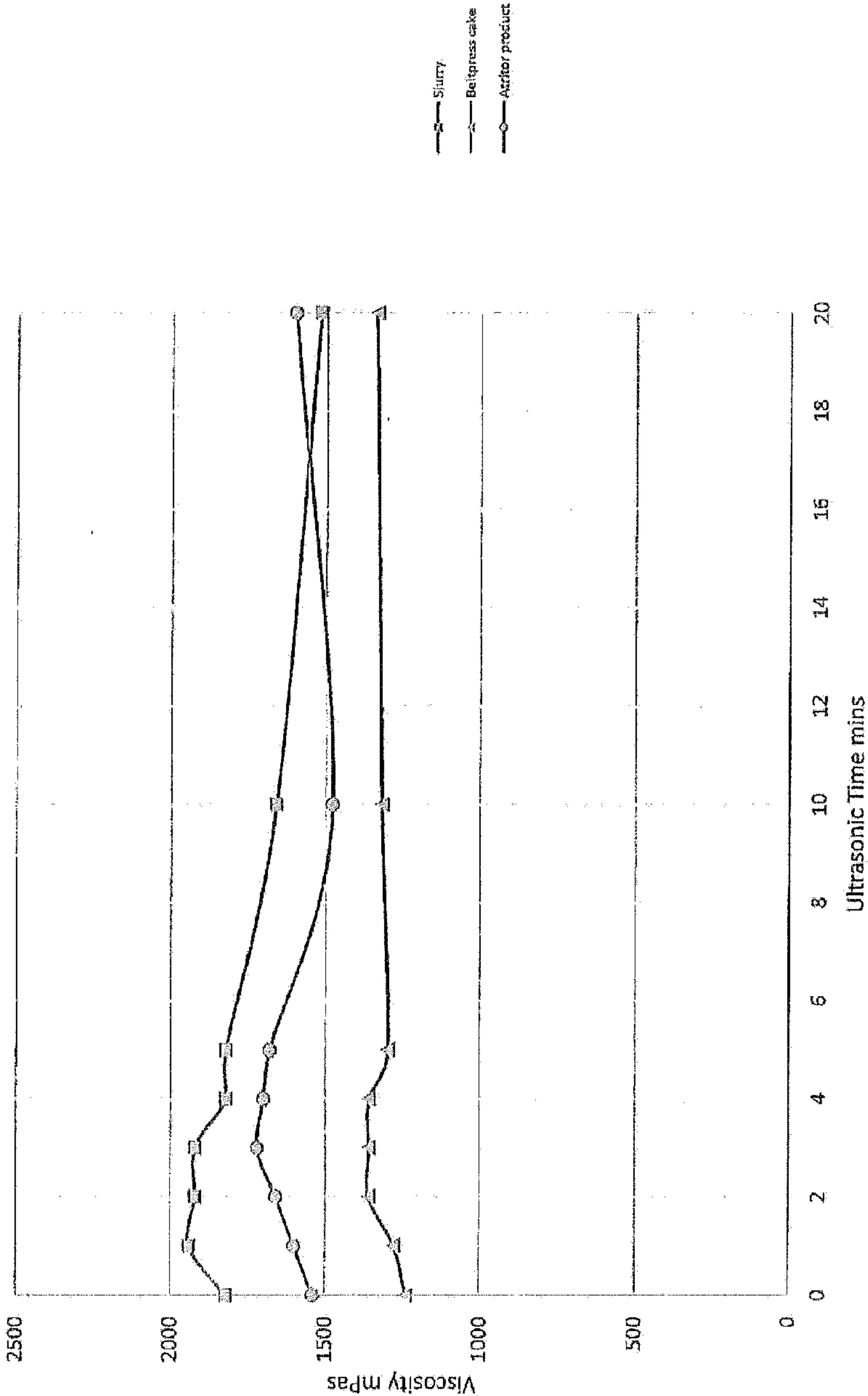


Figure 2

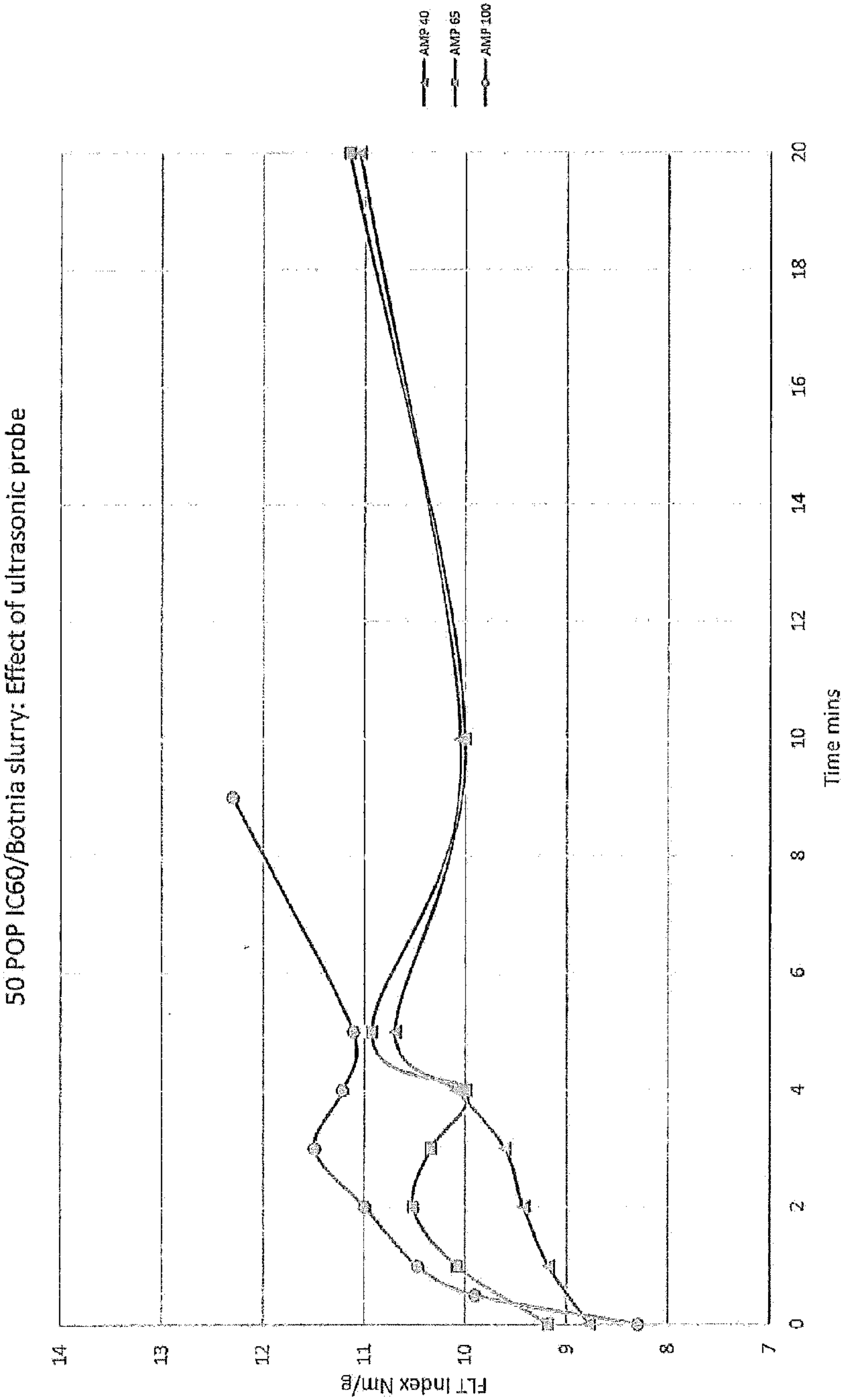


Figure 3

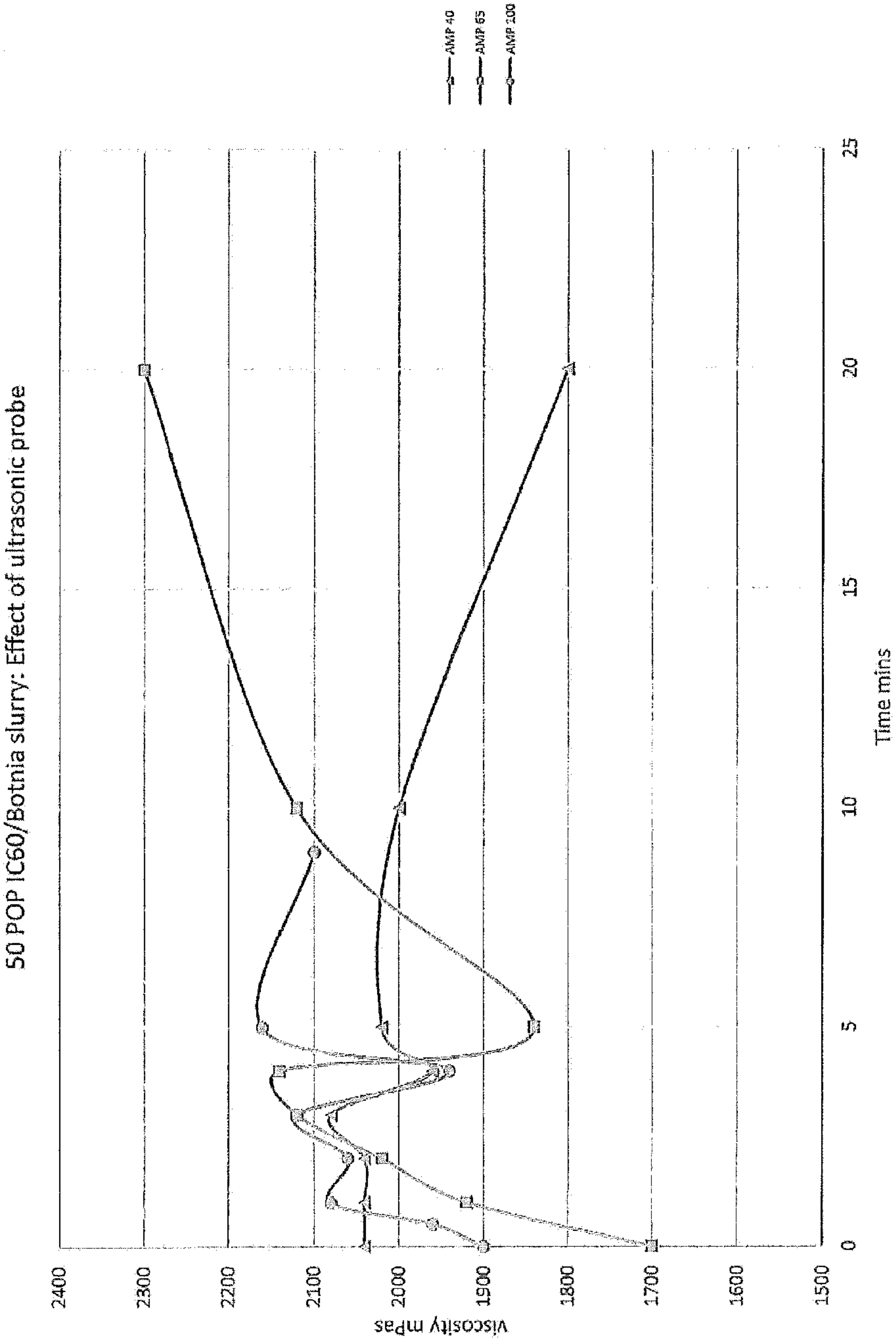


Figure 4

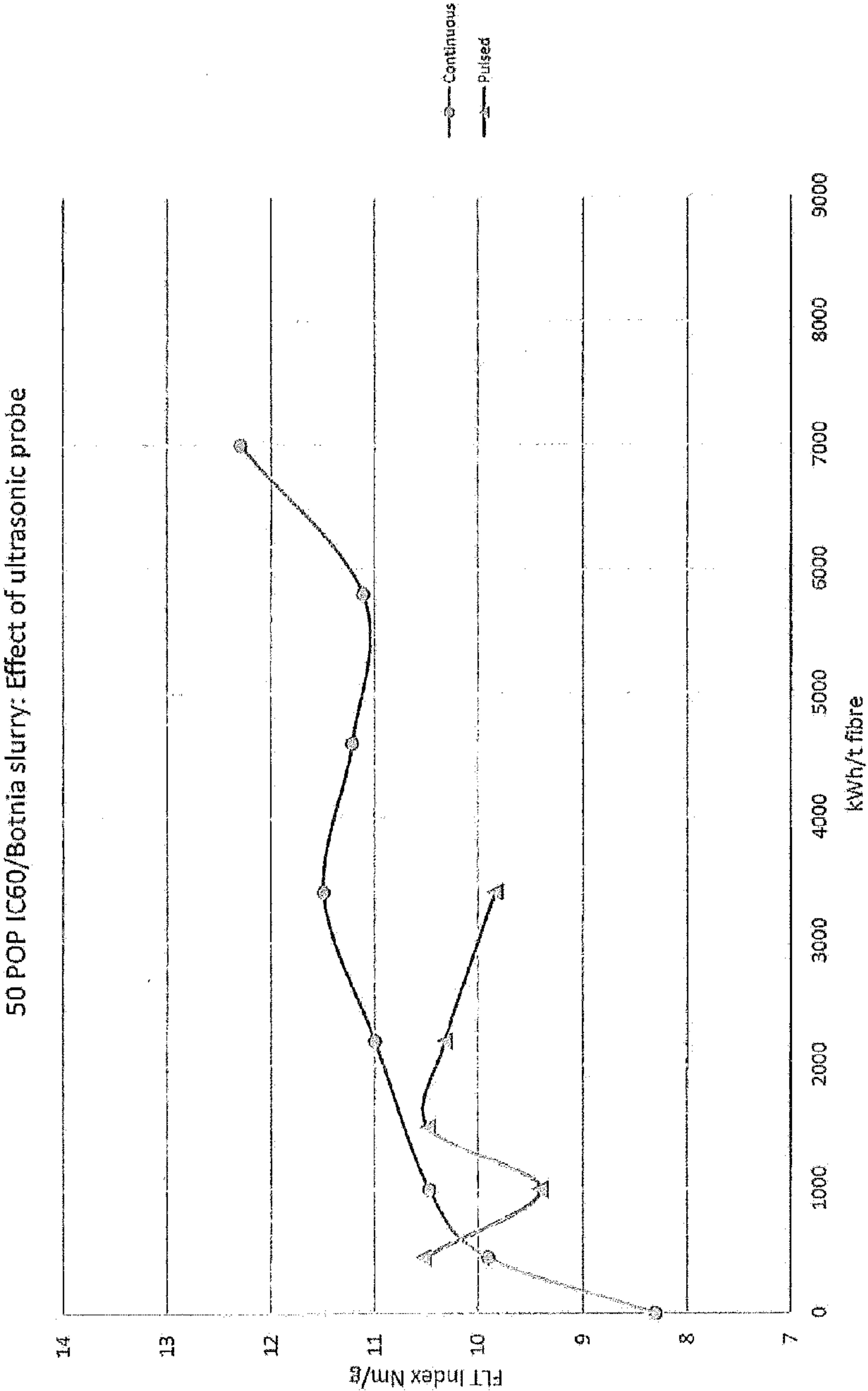


Figure 5

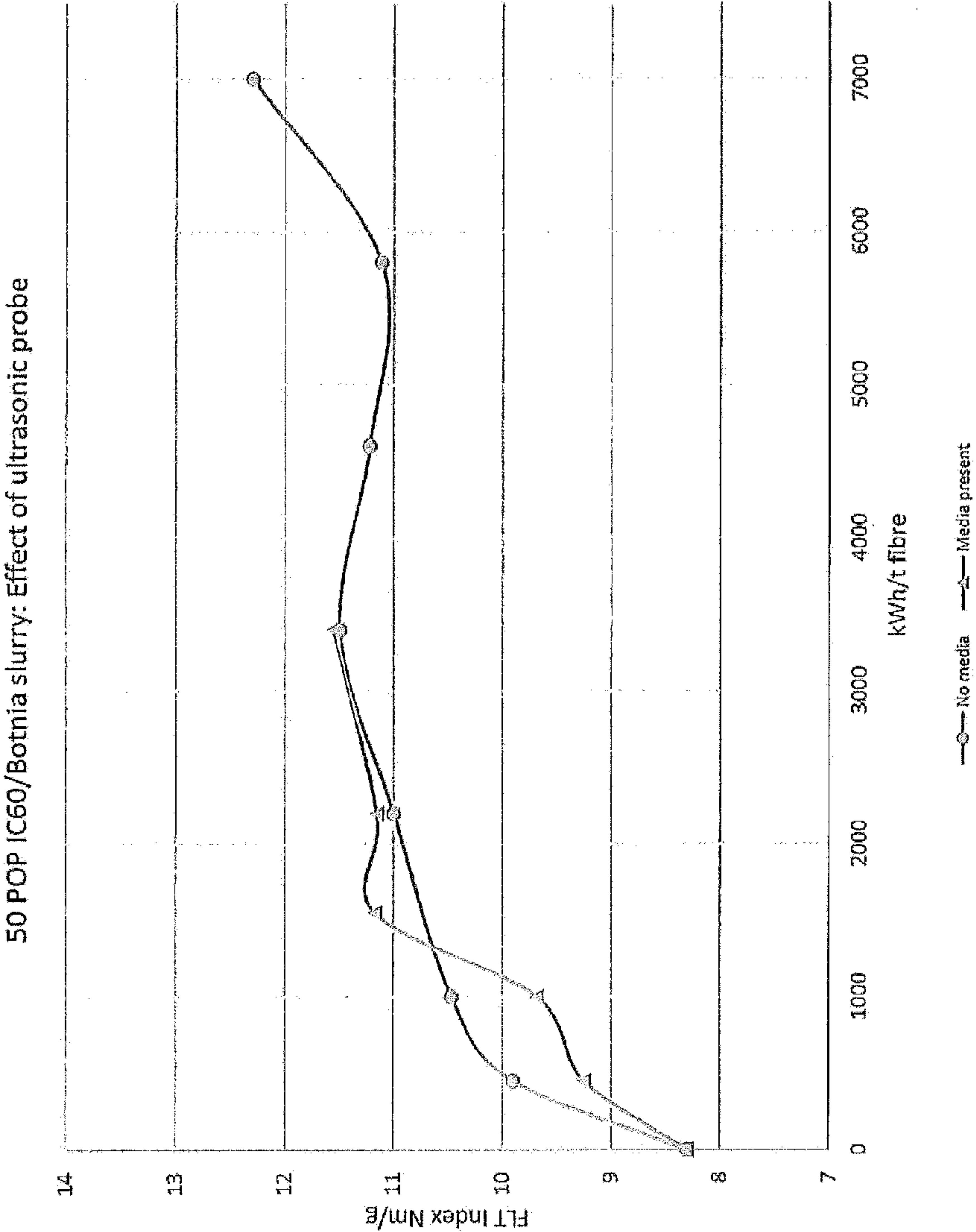


Figure 6

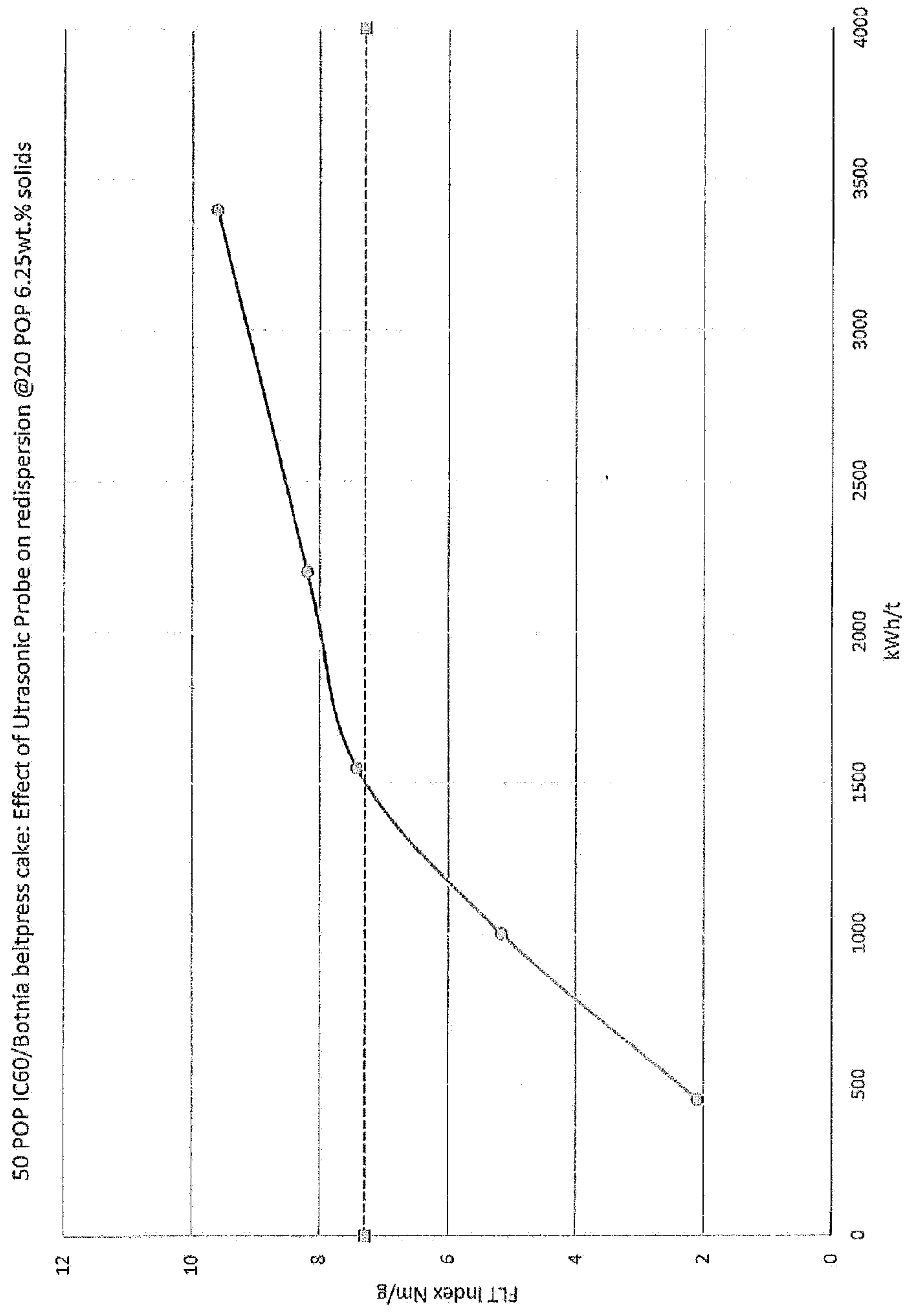


Figure 7

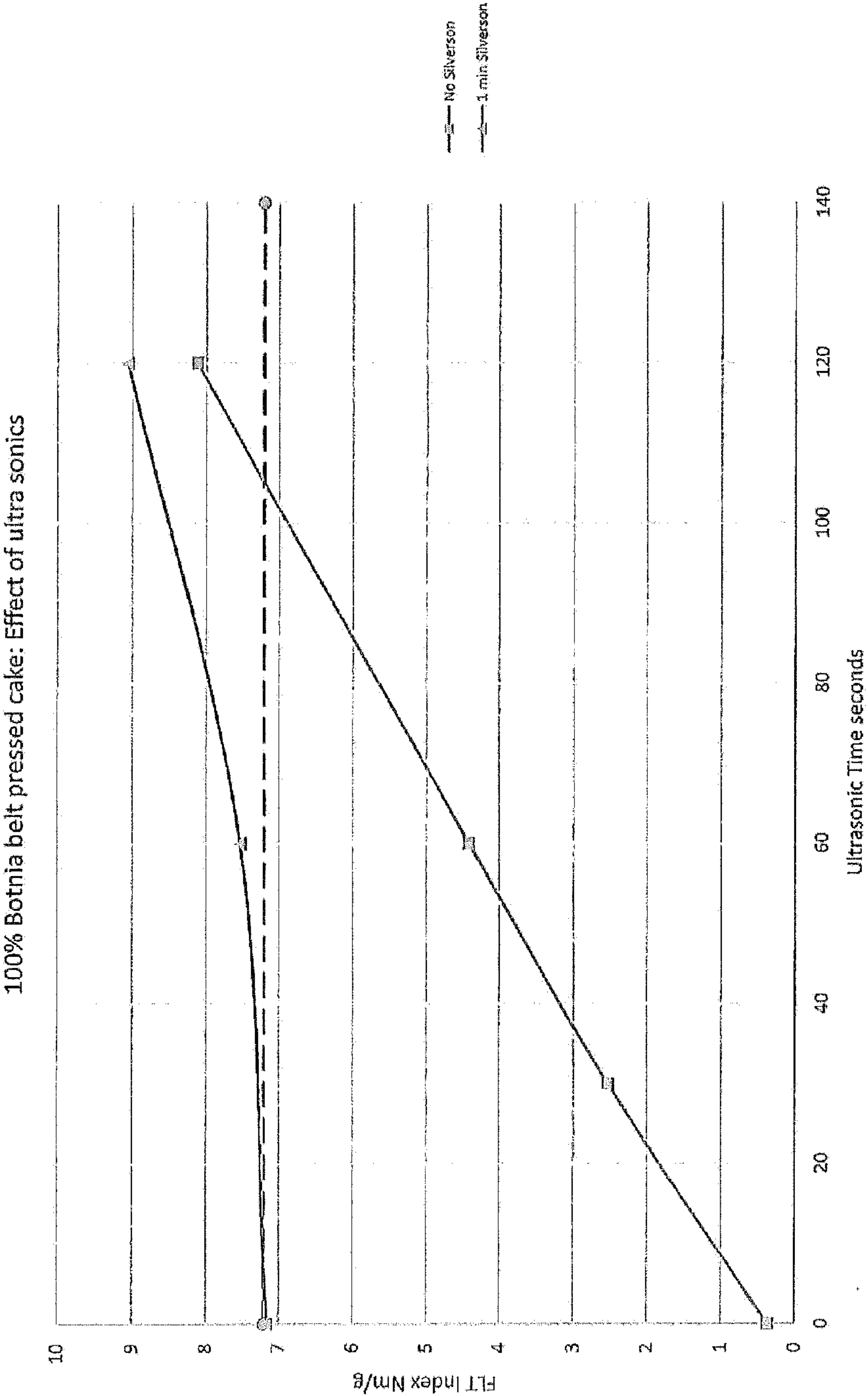


Figure 8

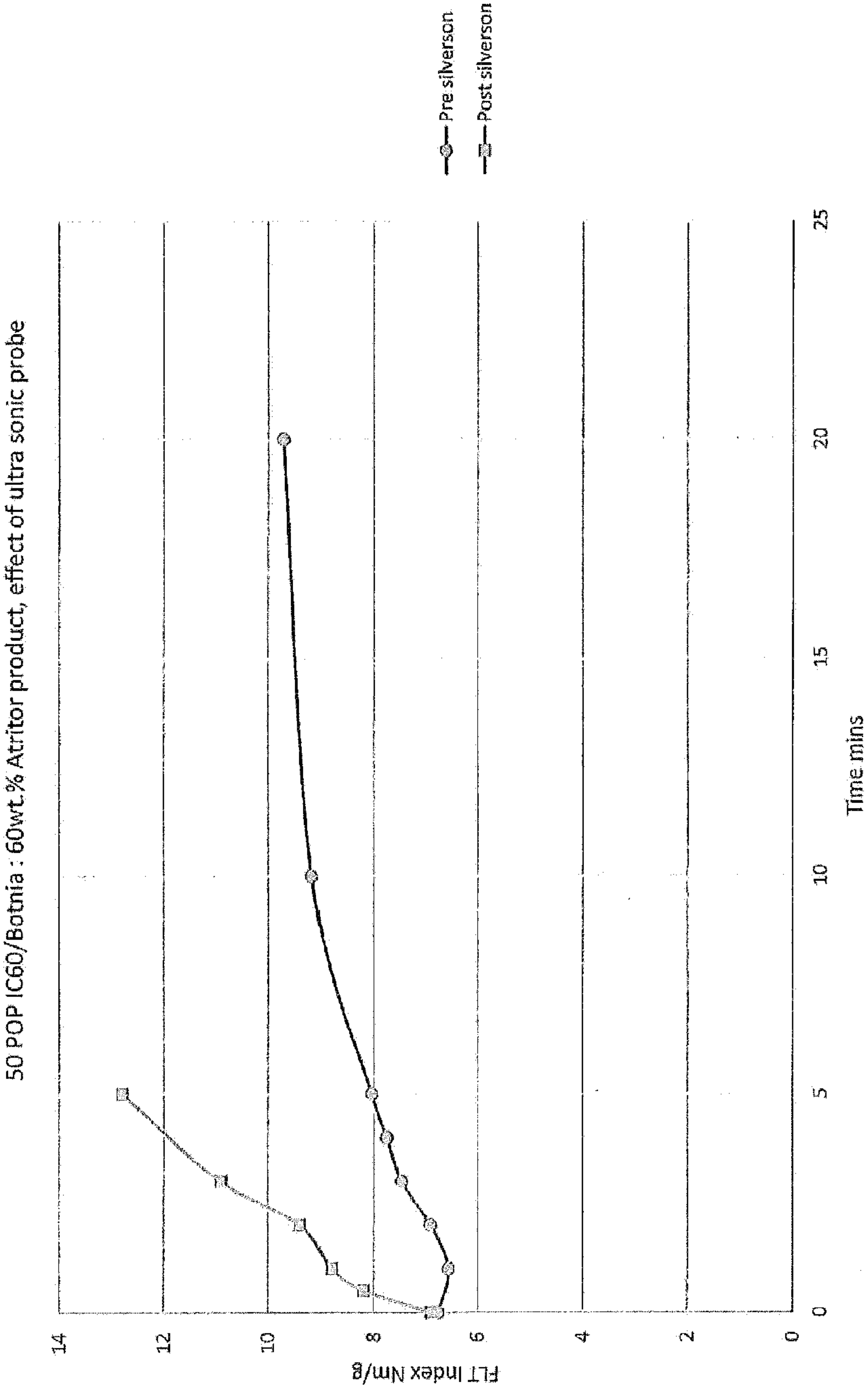


Figure 9

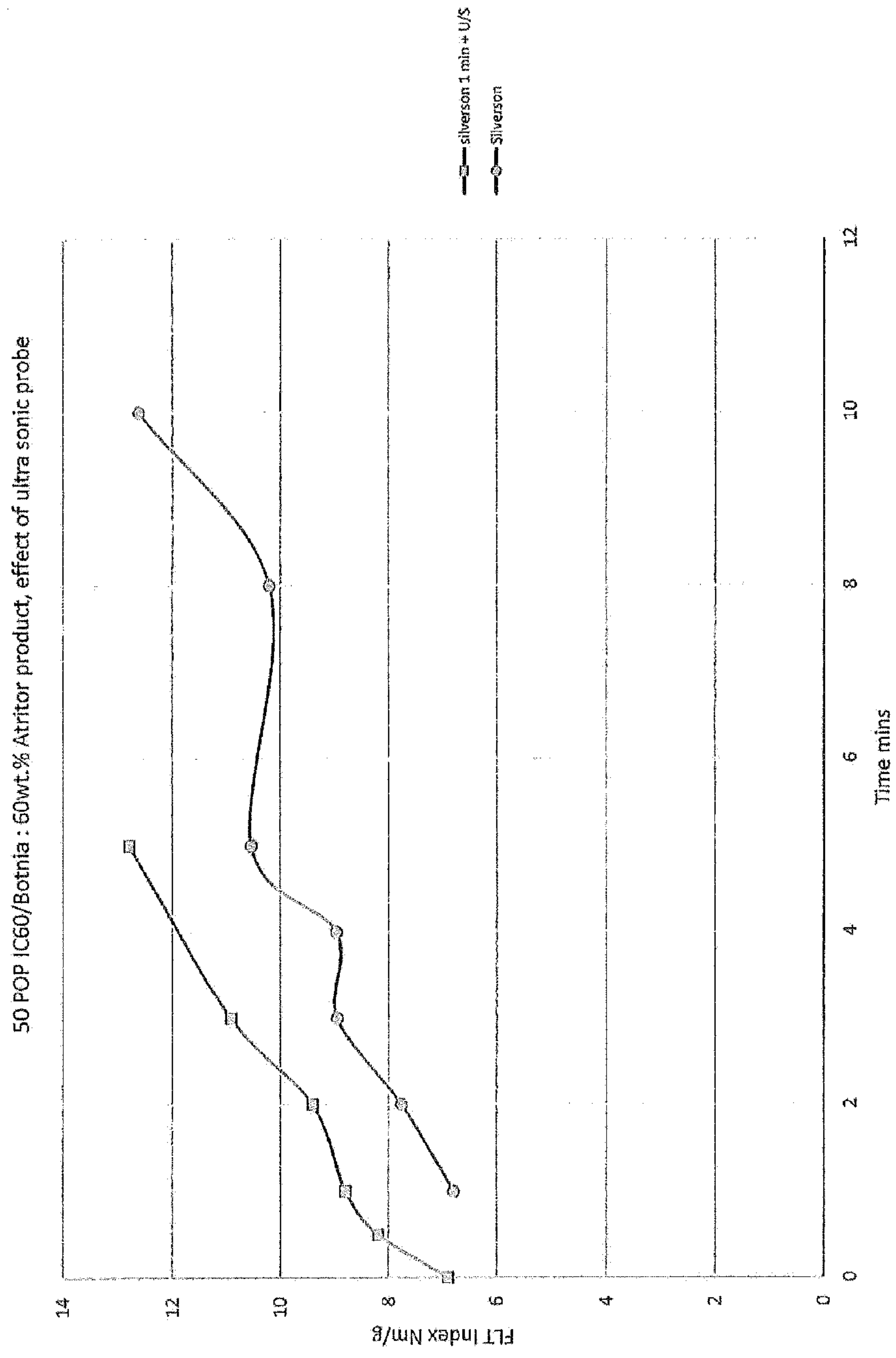


Figure 10

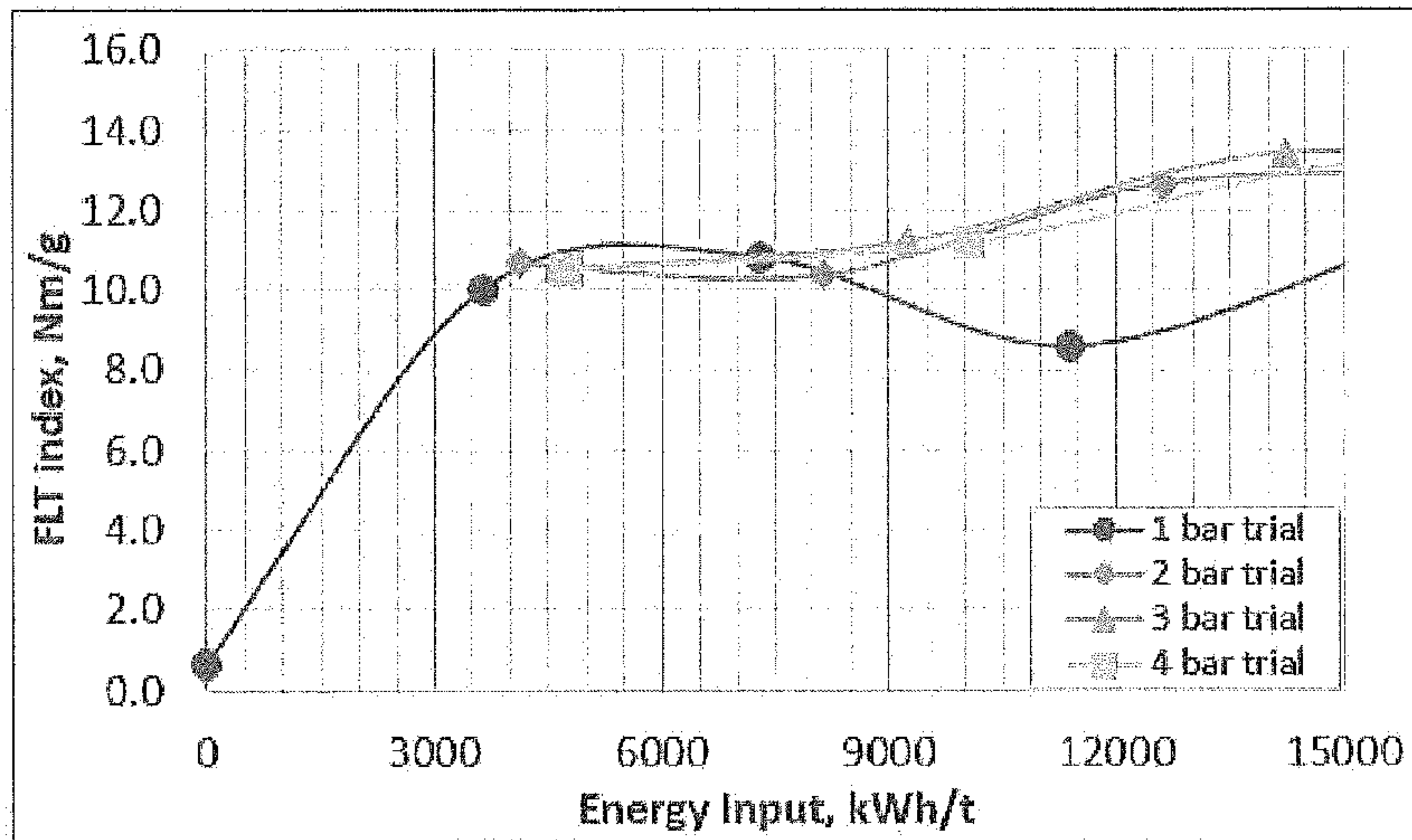


Figure 11A

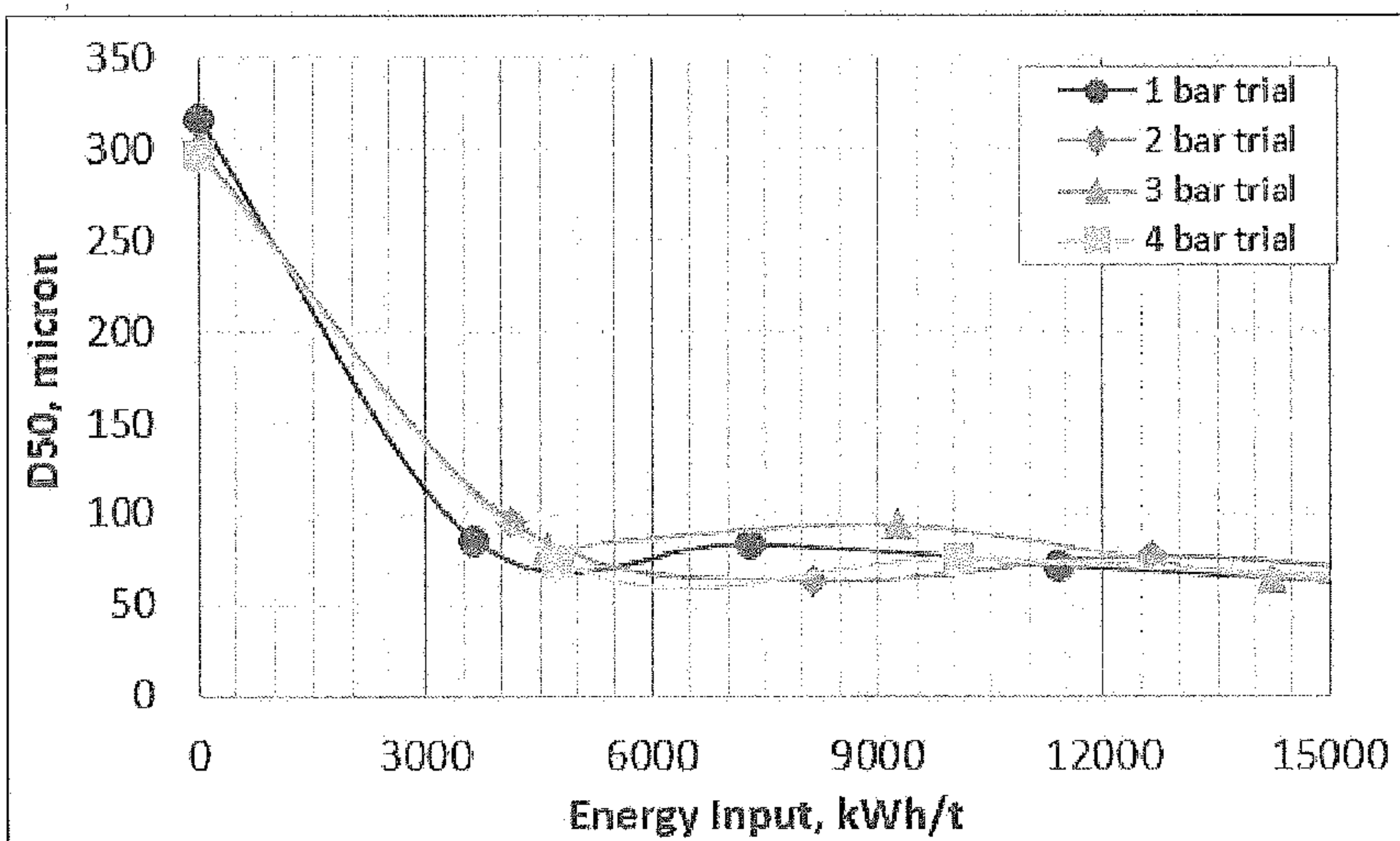


Figure 11B

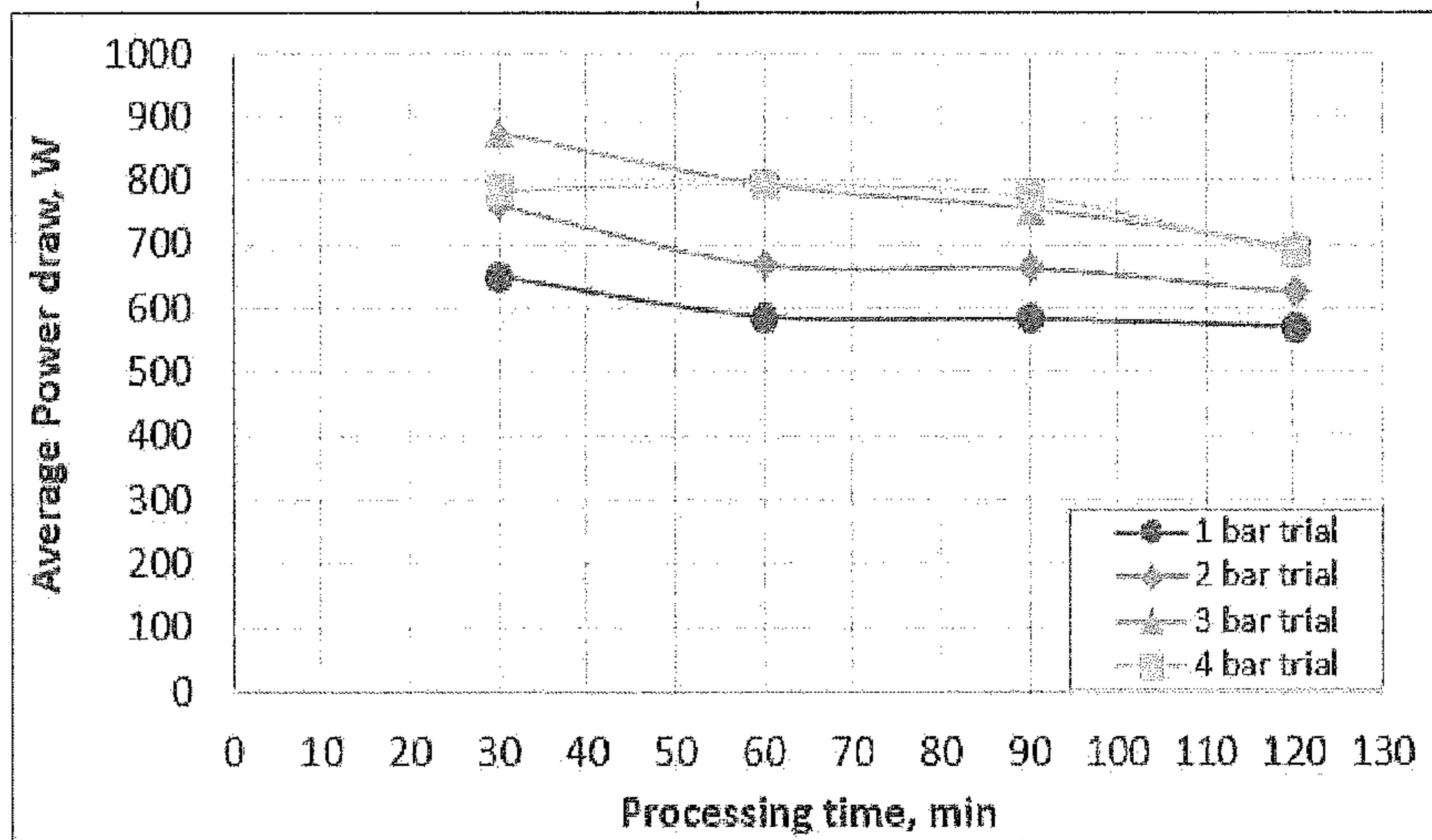


Figure 11C

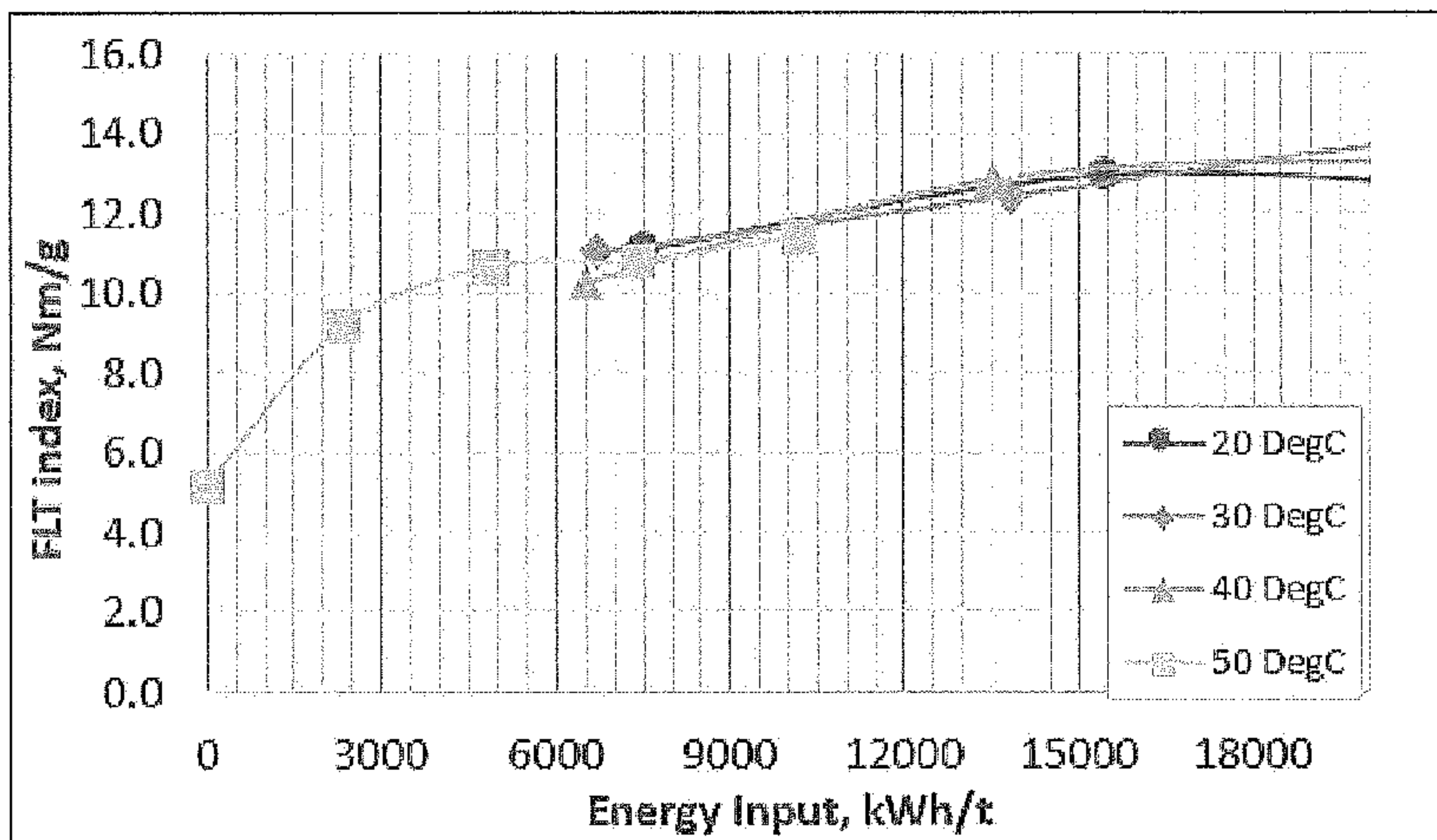


Figure 12A

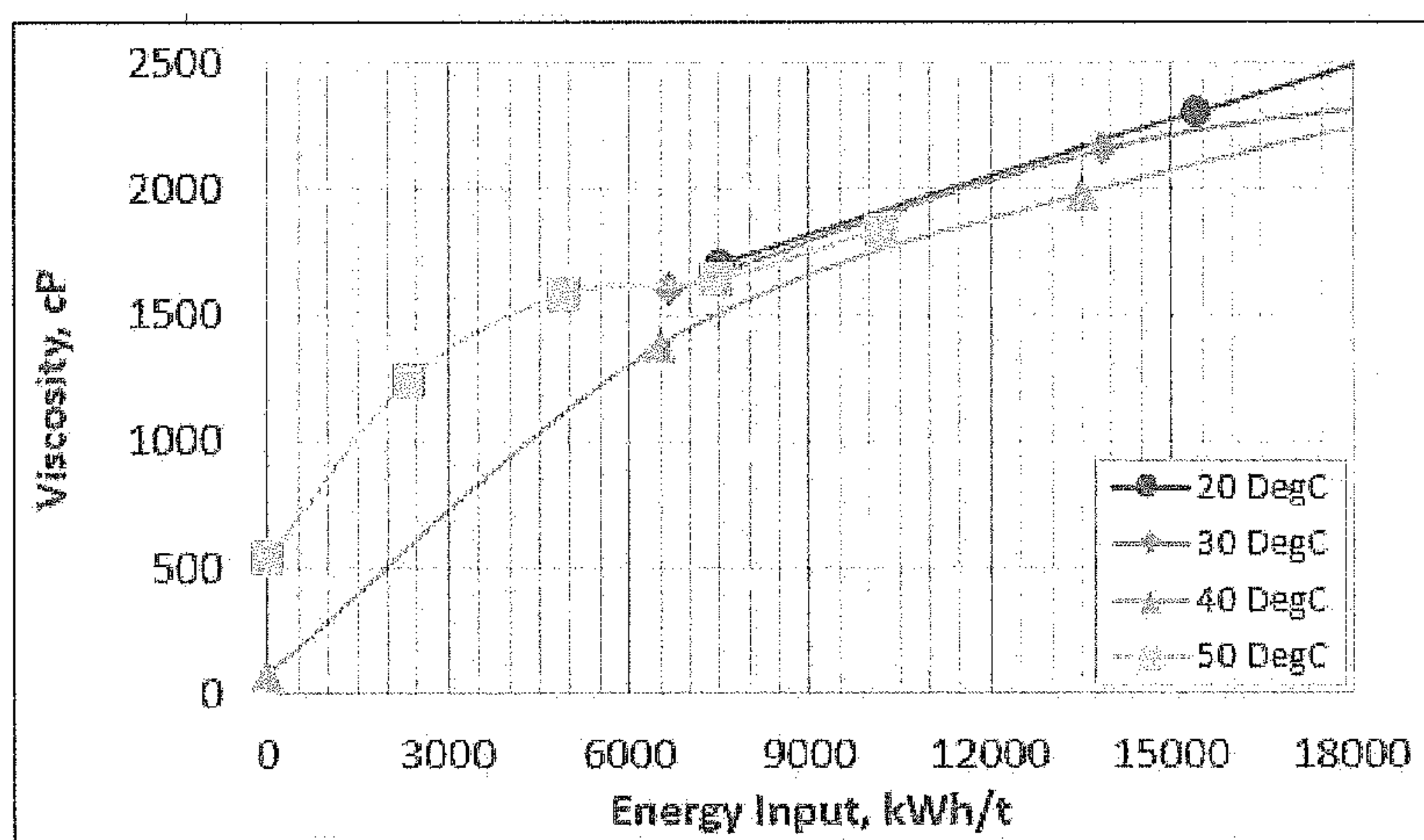


Figure 12B

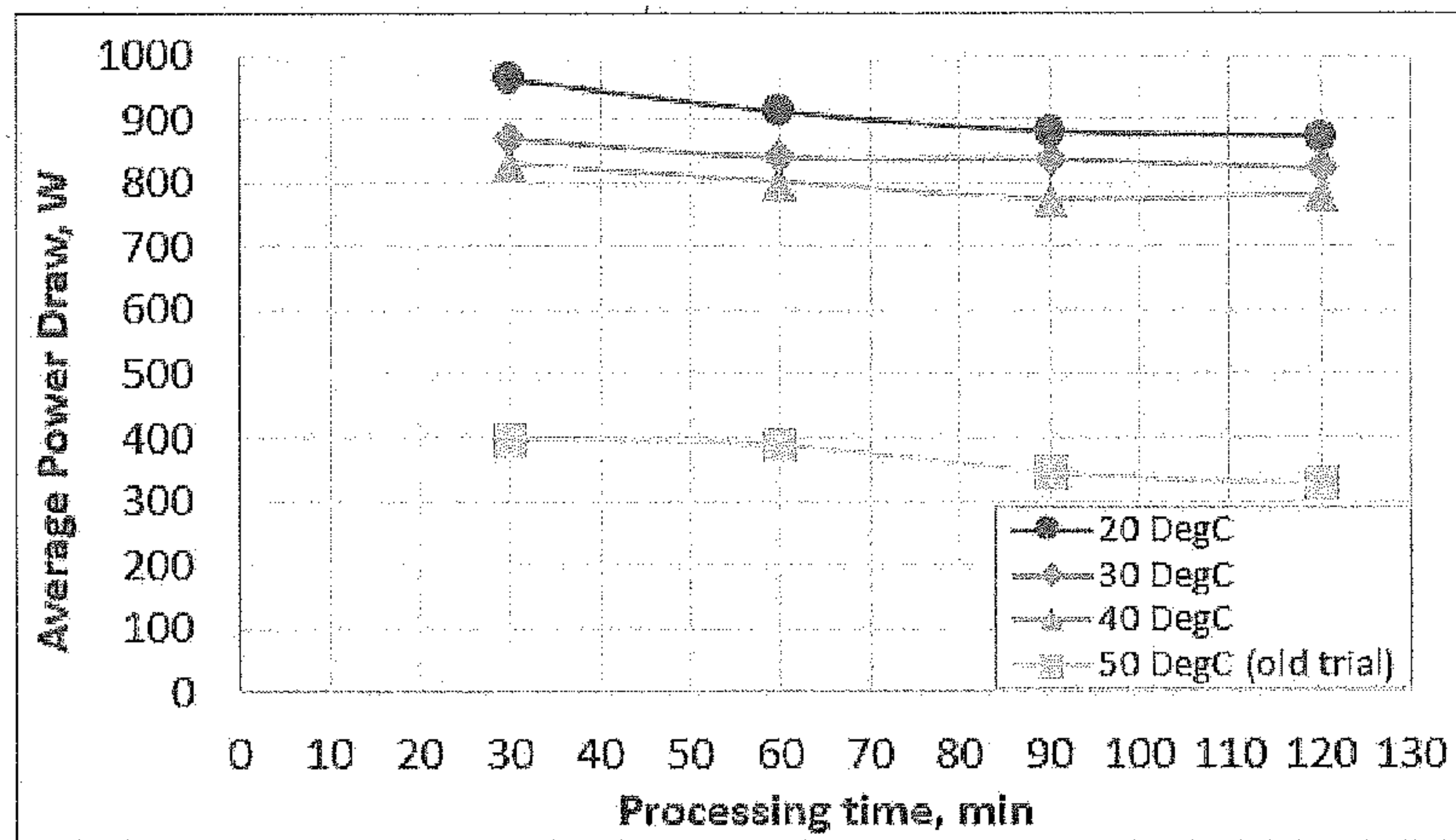


Figure 12C

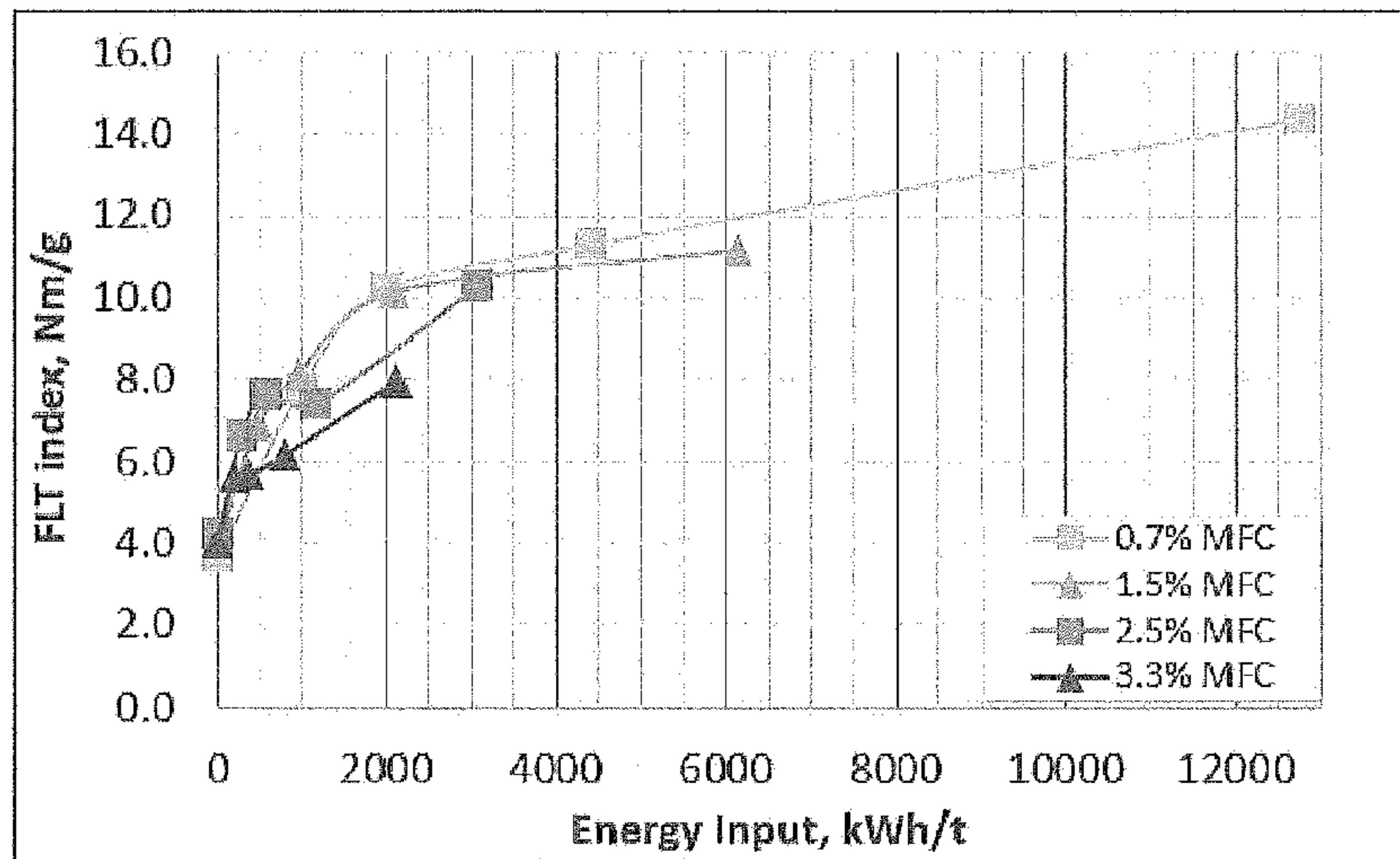


Figure 13A

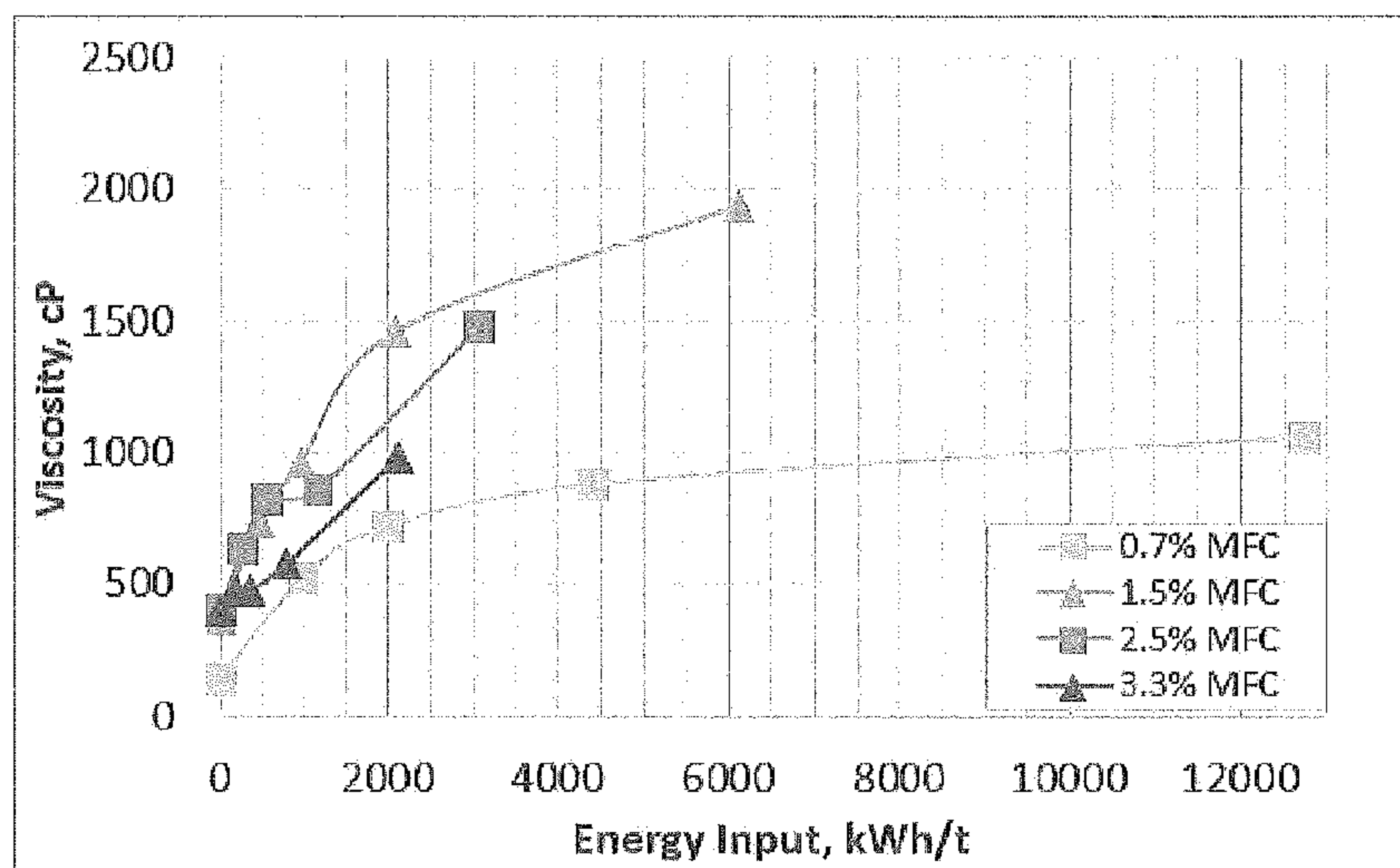


Figure 13B

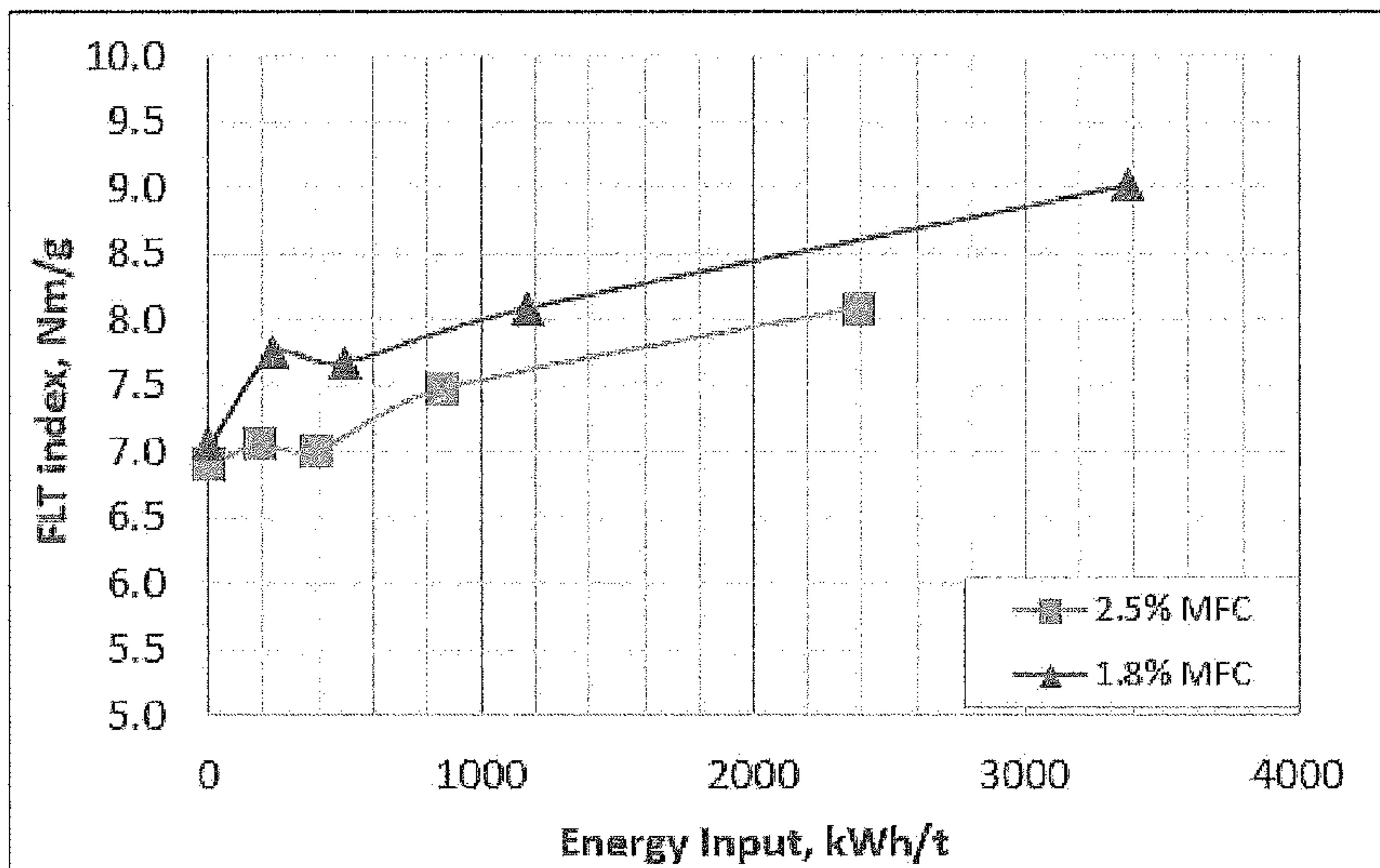


Figure 14A

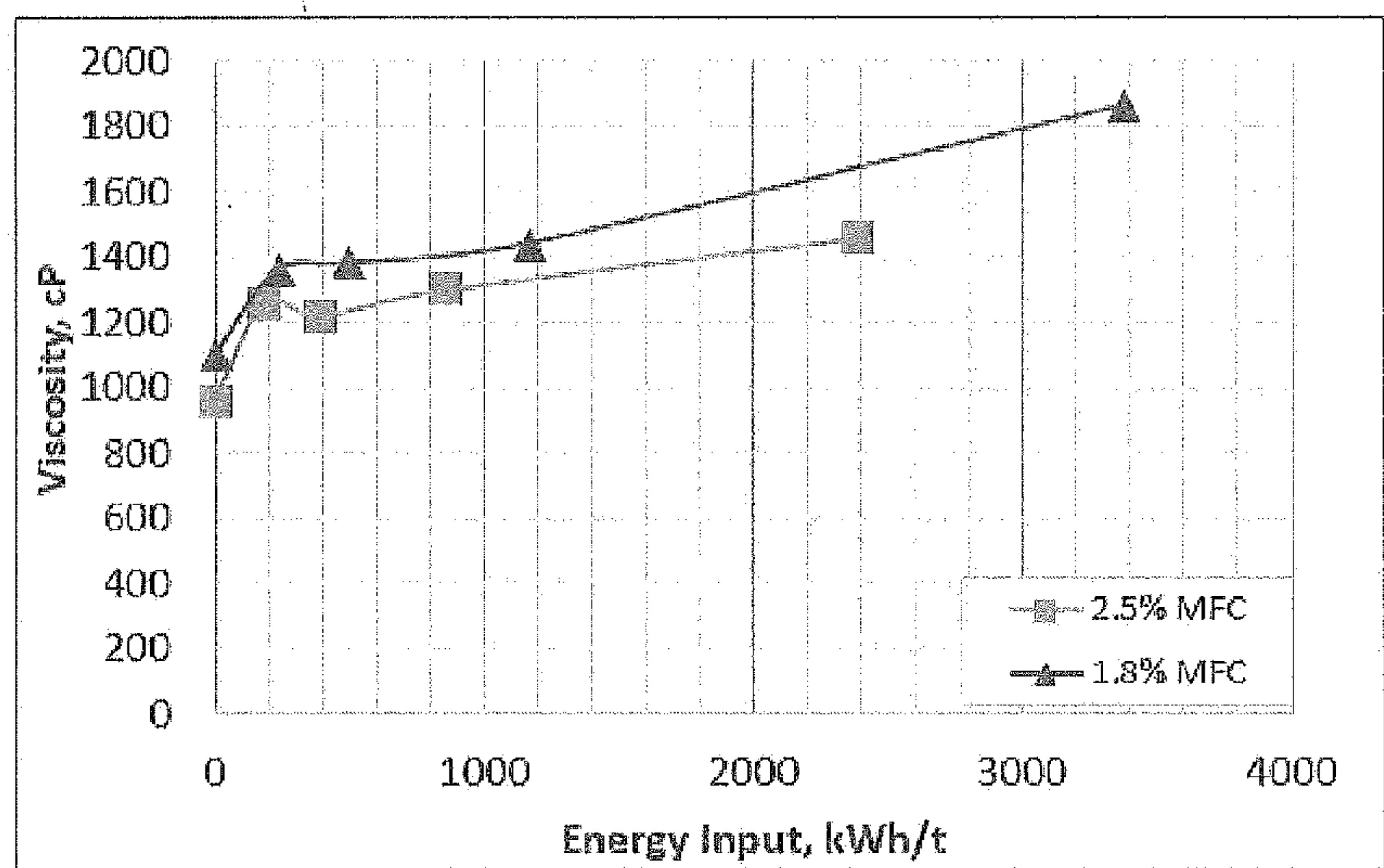


Figure 14B

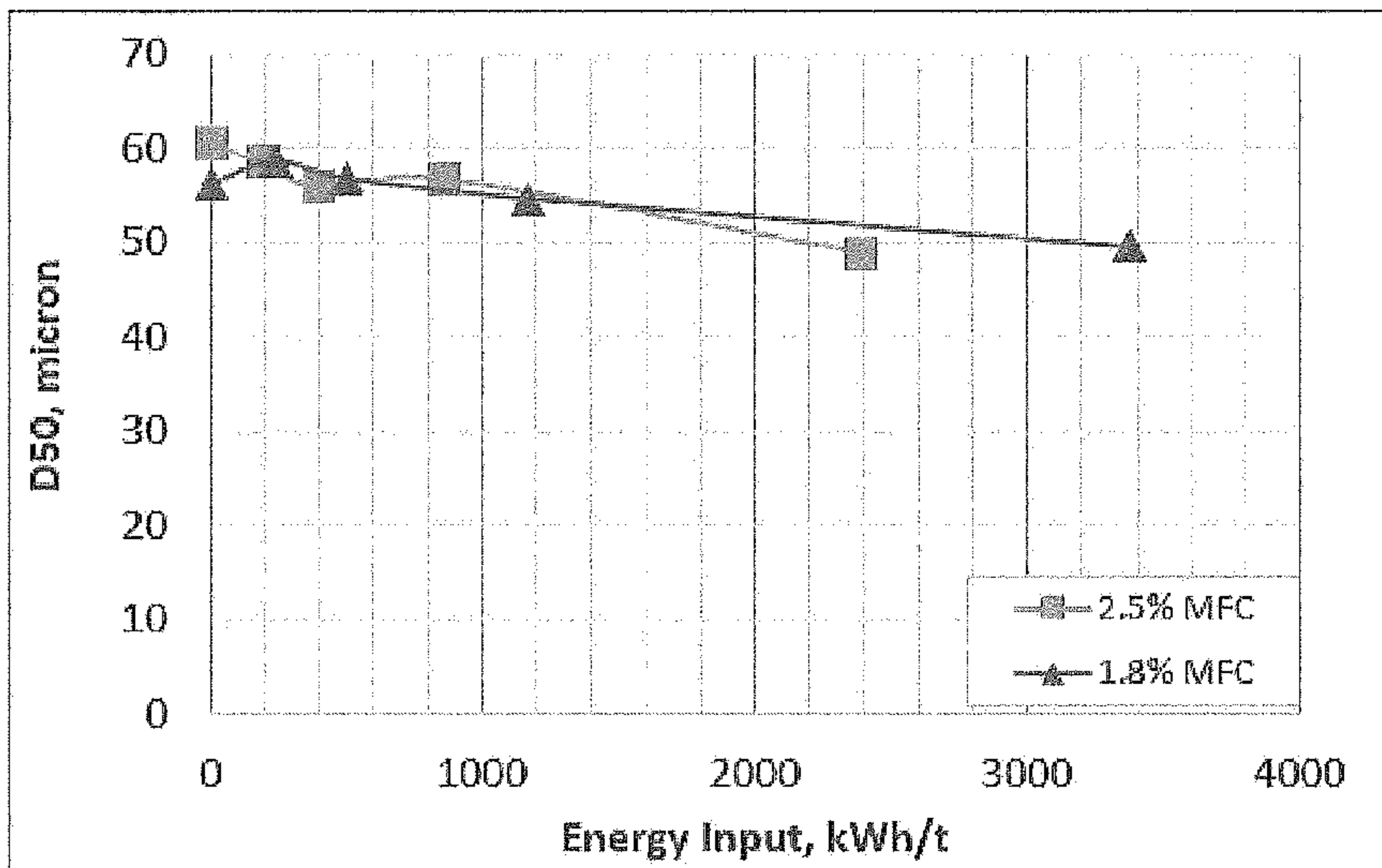


Figure 14C

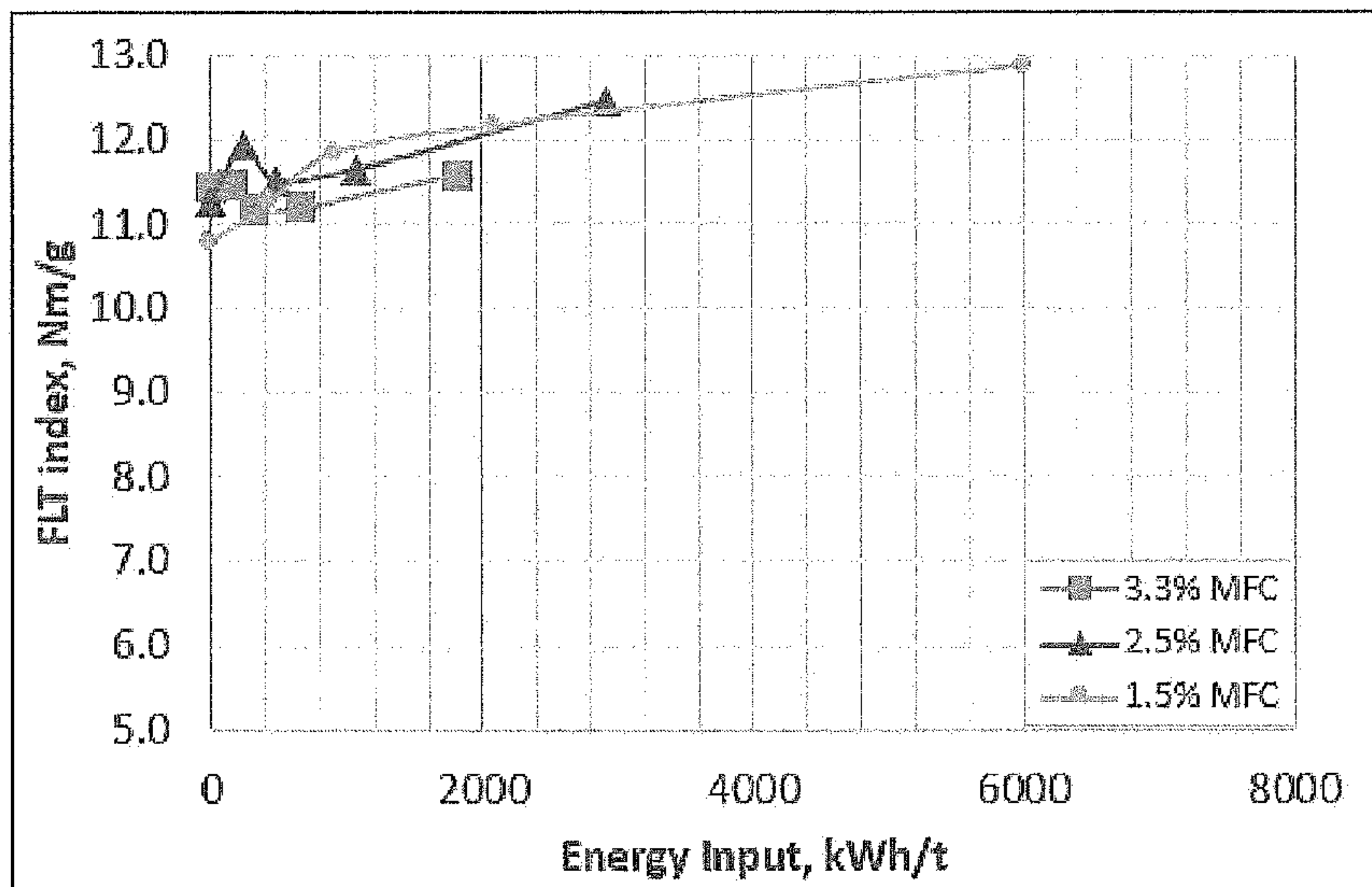


Figure 15A

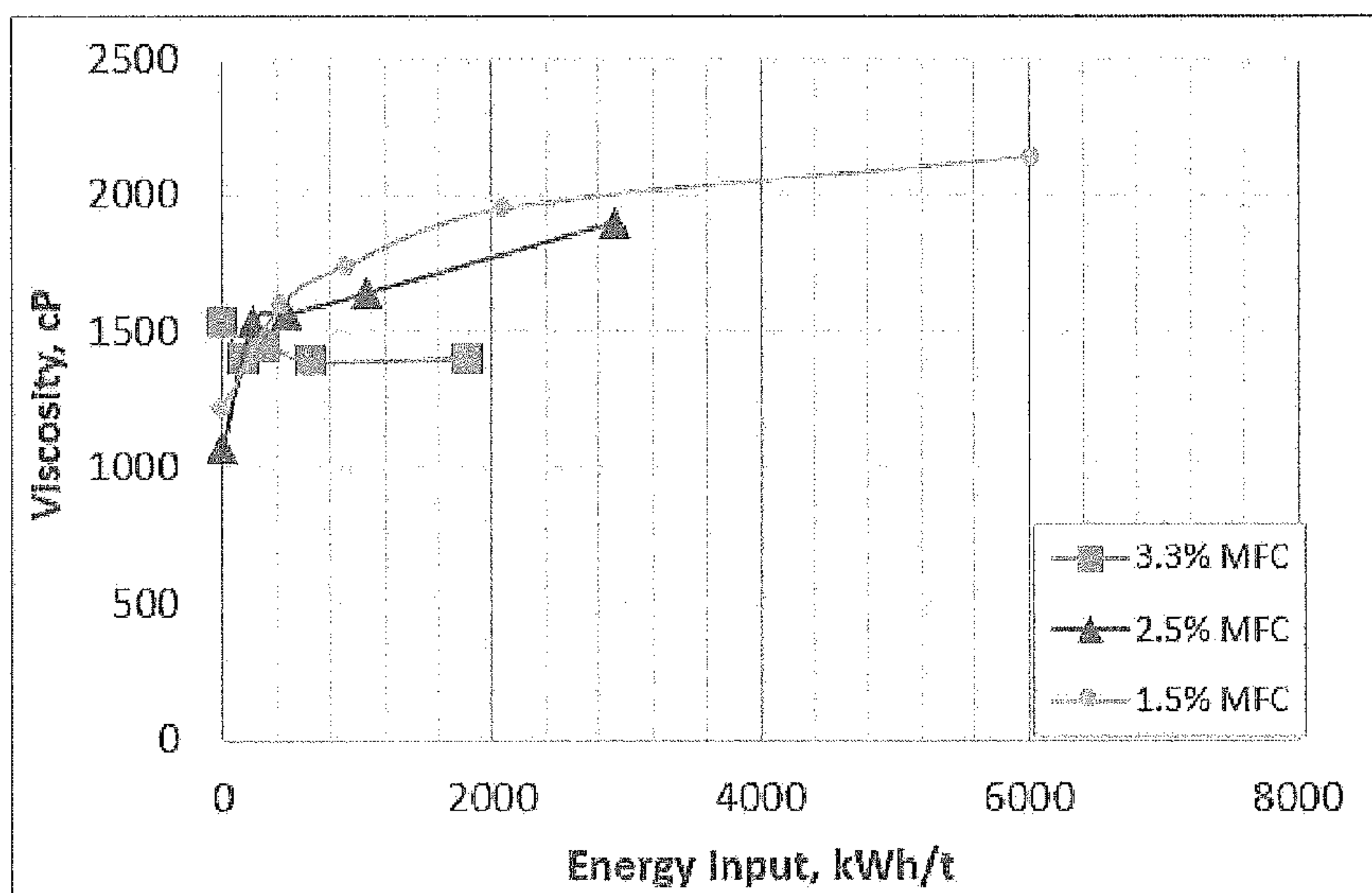


Figure 15B

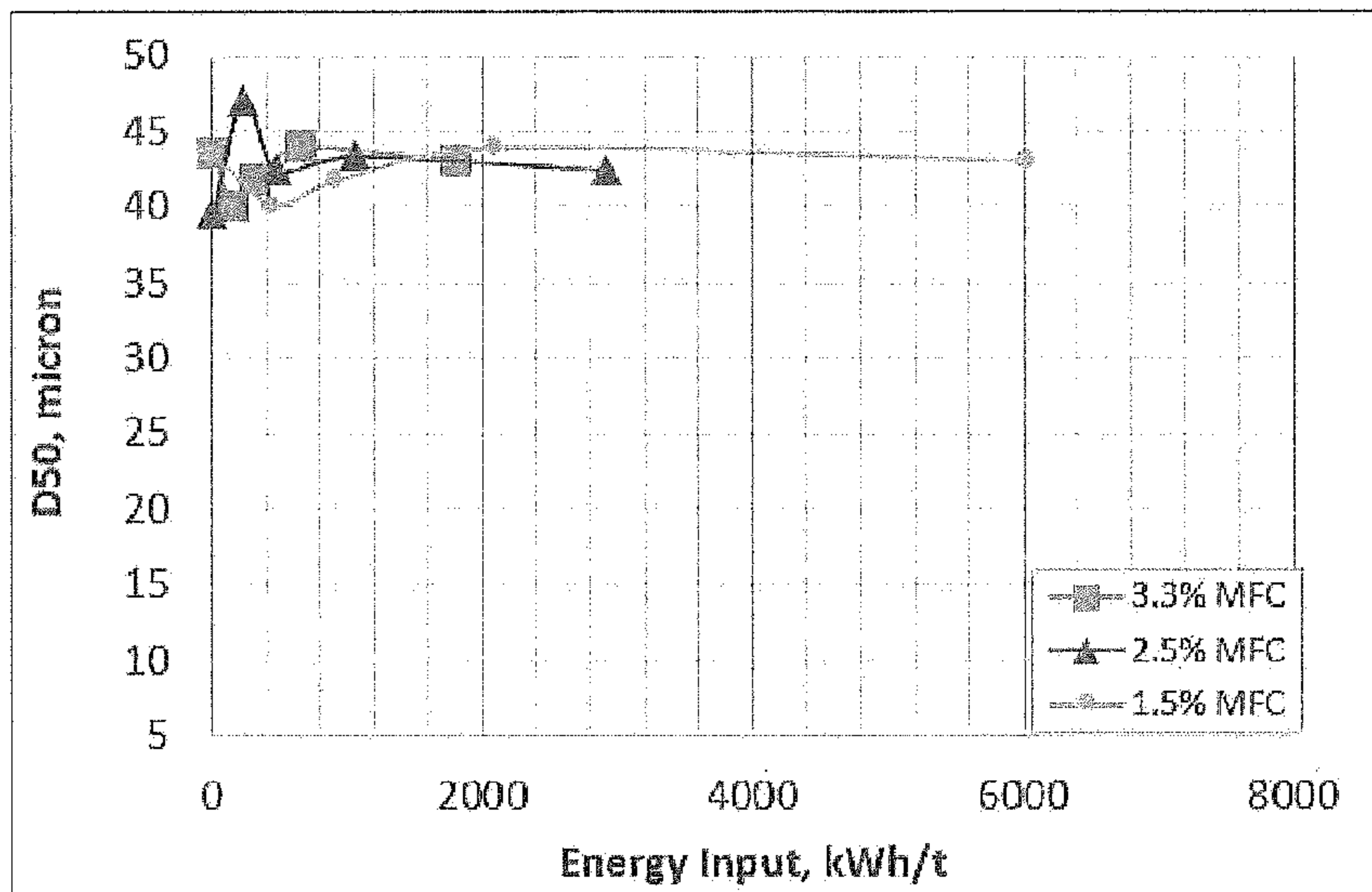


Figure 15C

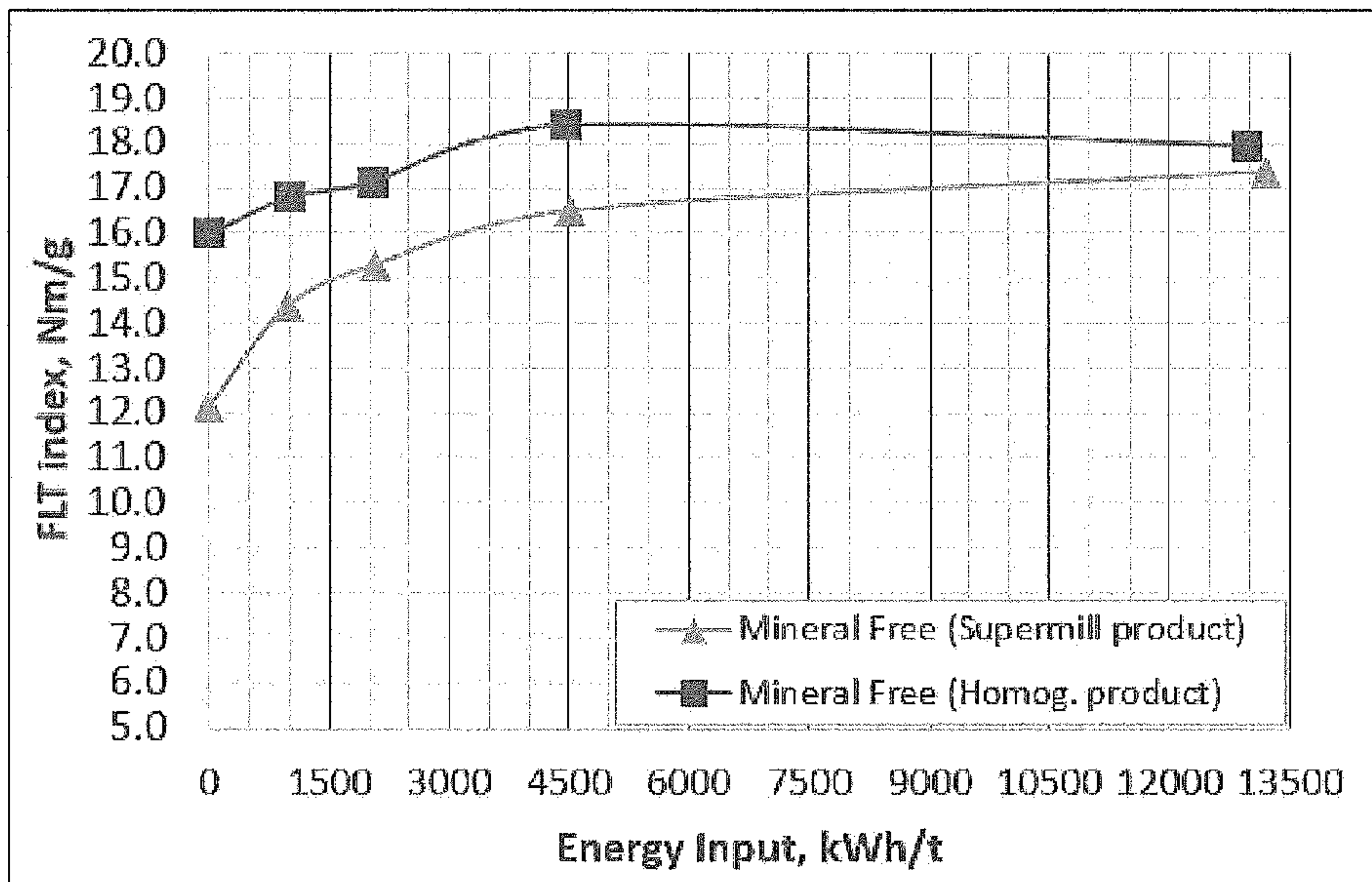


Figure 16A

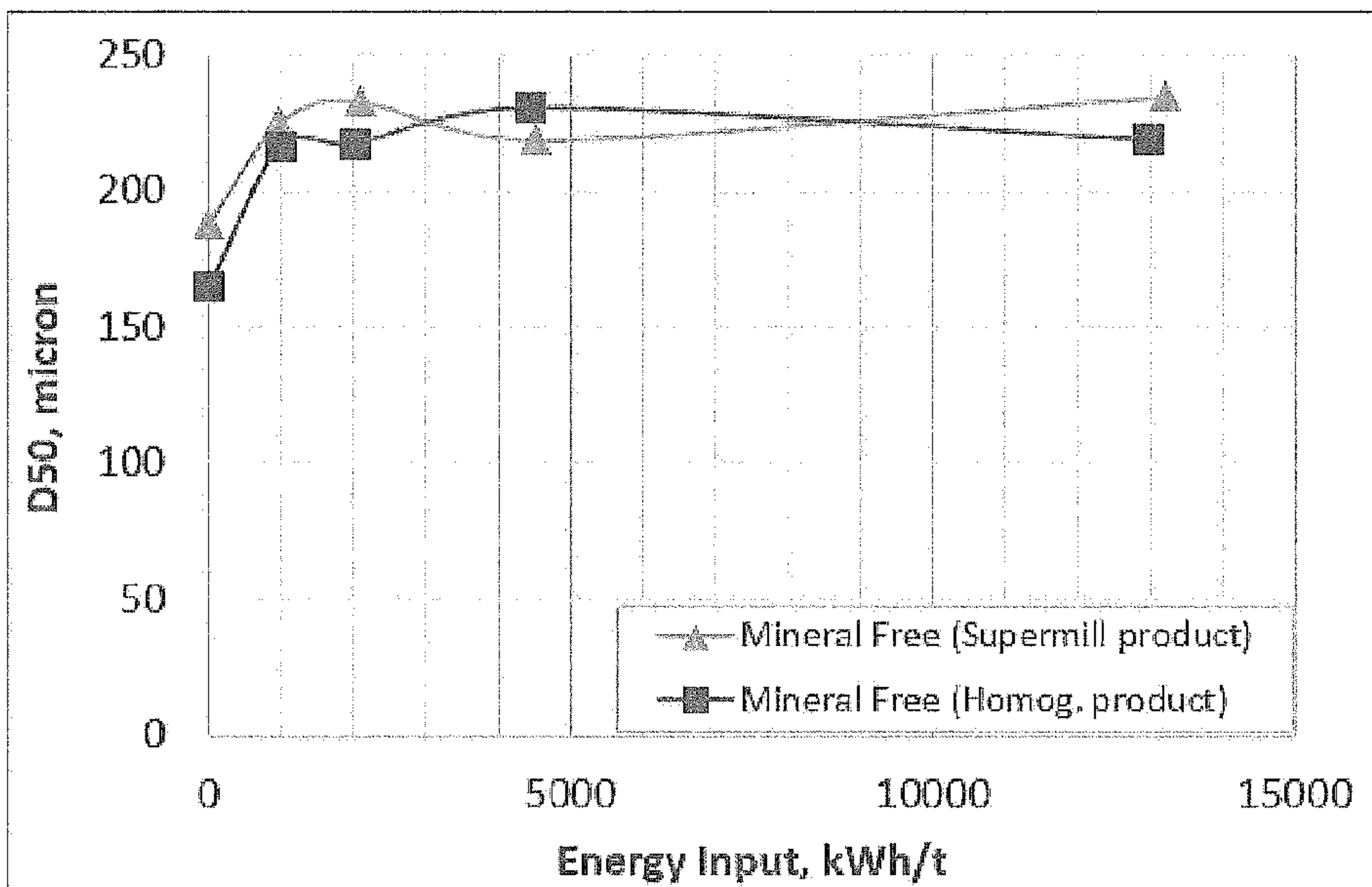


Figure 16B