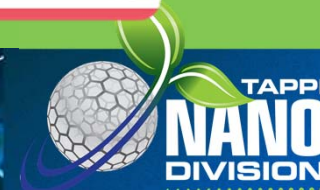


How to develop a particle size measurement standard for cellulose nanofibrils?

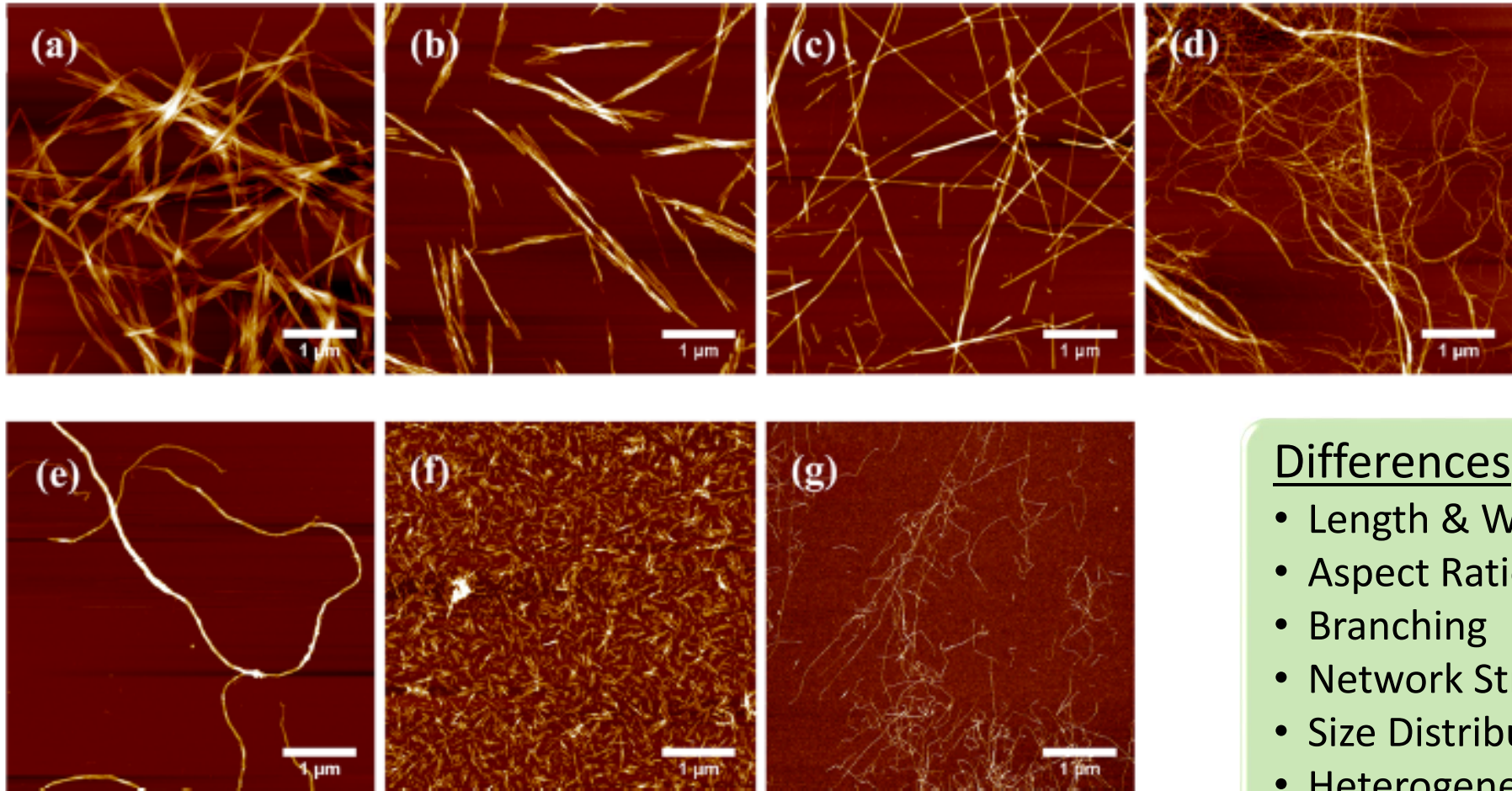
Warren Batchelor, Stephanie Beck, Julio Costa, Andreas Fall, Eiji Kojima, Cecilia Land Hensdal, Robert Moon, Colleen Walker



TAPPI Nano 2021 Virtual Conference
15-16 June 2021



CNMs – A Broad Range of Morphologies



Differences

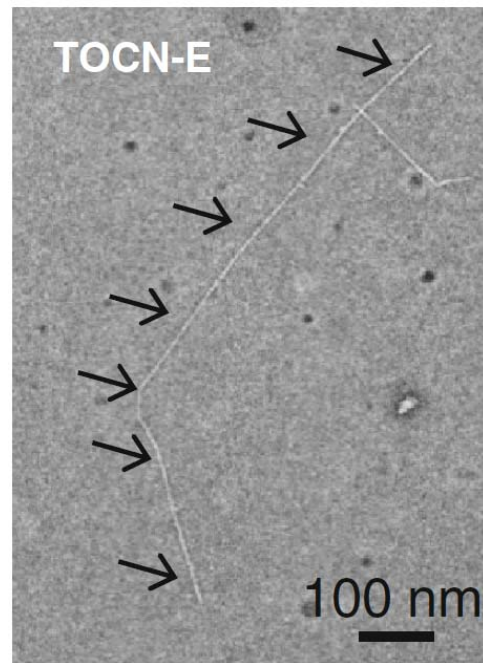
- Length & Width
- Aspect Ratio
- Branching
- Network Structure
- Size Distributions
- Heterogeneities

Different types of CNFs

Differences in Processing:

- Pretreatments
 - Enzymatic
 - Chemical
- Fibrillation Process
 - Microfluidizer
 - Homogenizer
- Fractionation

Individualized CNF



Entangled CNF

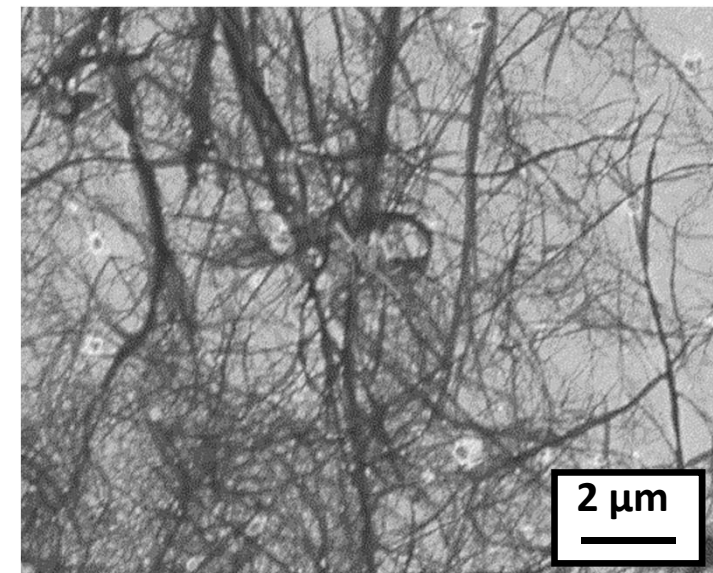


Image by GeorgiaTech

Tanaka, R., Saito, T., Ishii, D., & Isogai, A. (2014). *Cellulose*, 21(3), 1581-1589.

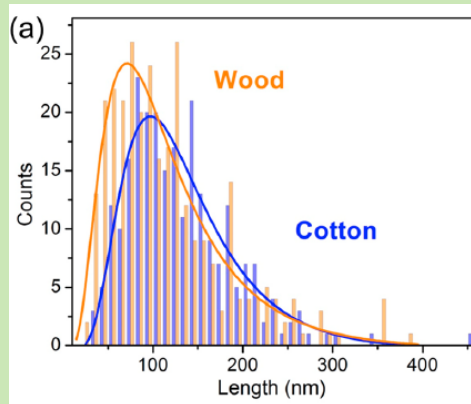
Particle Size & Distribution Measurements

Particle Size

- Length, width, aspect ratio
- Branching

Distribution

- More than just the mean



Techniques

- Image Analysis
 - Optical
 - SEM, TEM, AFM
- Scattering etc.
 - DLS – Dynamic Light Scattering
 - Laser Diffraction Analysis
 - Transmittance
 - Turbidity
- Fractionation
 - Centrifugation
 - Asymmetric Field Flow Fractionation

Different needs for....

Quality Control



Materials Specifications



Health & Safety

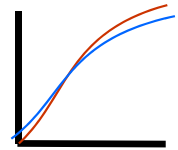


- Environmental
- Occupational

Research



- Measurement
- Protocols



Lab I = Lab II

Needs?

- Standards
- Technical specifications
- Measurement guidelines

CNM Standards Development Task Group

ISO /TC 6 – Paper, Board & Pulps

- **TG 1** – Cellulosic Nanomaterials
 - Tasked to assess standards needs
 - Recommend updates to existing standards
 - Identify new standards to develop
 - ISO/TC 6 & ISO/TC 229

- Surveying industry needs



The ISO/TC 6 /TG 1 –...CNF Particle Measurement Team

- Warren Batchelor
- Stephanie Beck
- Julio Costa
- Andreas Fall
- Eiji Kojima
- Cecilia Land Hensdal
- Robert Moon (Convenor of TG1)
- Colleen Walker

How to know which PSD standards are needed?



Survey

- Producers, Users, Equipment Manufacturers & Researchers
- Scope focused on CNF particle size measurement
- Online, anonymous format

Communication & Discussion Events

- TappiNano presentation, June 2020 (Colleen Walker)
- Particle Size Webinar hosted by TAPPI, August 2020
- Keynote talk at the ABTCP conference, October 2020 (Robert Moon)
- Workshop, June 2021, with group discussions



SURVEY DESIGN

Two Groups

Japan – Coordinated by Japan TAPPI & Nanocellulose Japan

Global – (minus Japan) Coordinated by ISO/TAPPI Nano Division

Questions

A. Respondent Information

Research institute or commercial company?

If company, which sector?

Which category of CNF development?

B. CNF Processing

What pretreatment is used?

What is the final fibrillation step?

What is relative liquid content in final CNF?

What is the relative level of dispersion?

Questions

C. Particle Size Measurement

Particle size standard needed for?

Which dimensions are needed?

Measure in wet or dry state?

Allow for salts and additives in the sample?

Which dimensions need size distribution?

What type of size distribution information?

Are you currently measuring particle size?

What techniques are used?

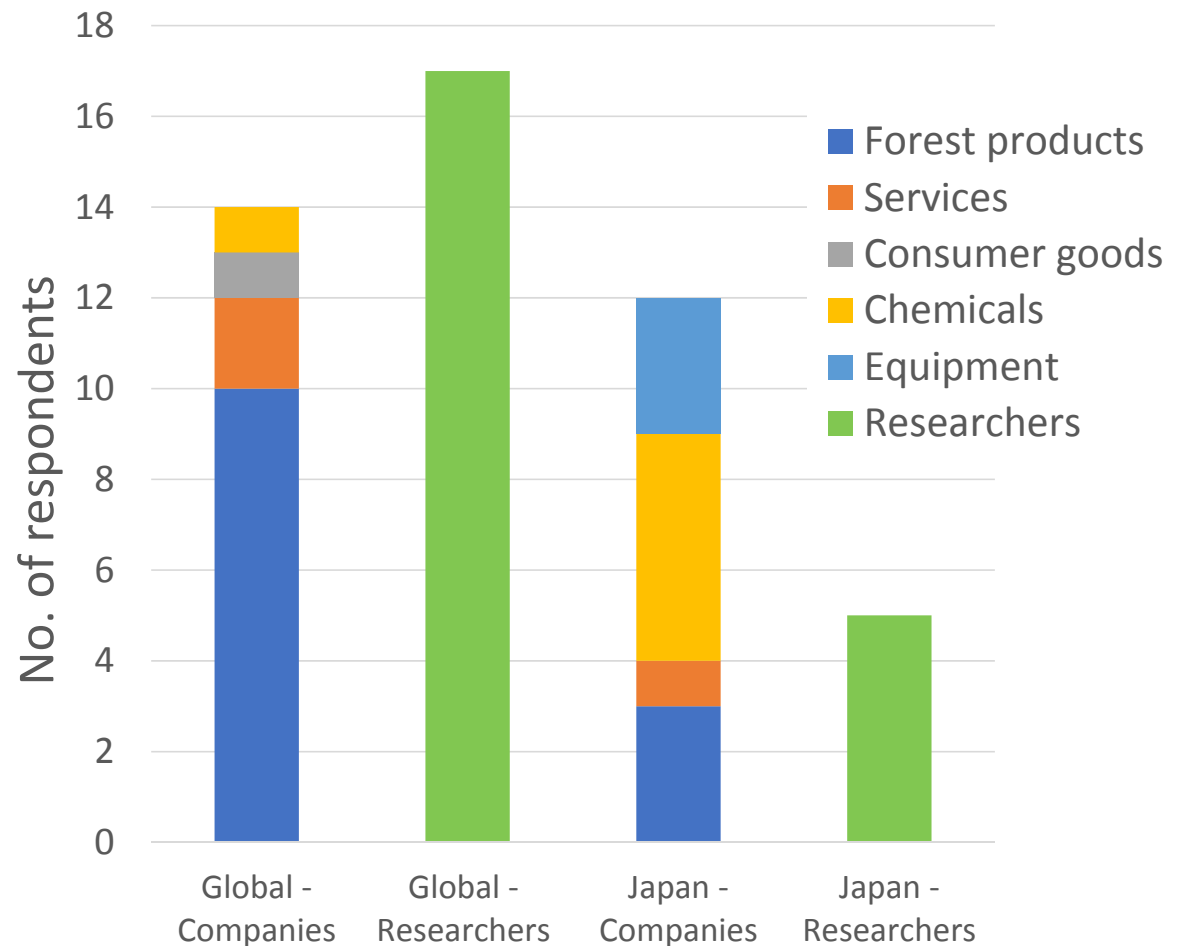
A. Respondent Information

Response: 48

- Global 31
 - Companies 14
 - Researchers 17
- Japan 17
 - Companies 12
 - Researchers 5

Key Points

- Global
 - More researchers responded
 - Forest products dominate
- Japan
 - More companies responded
 - Variety of product categories



B. CNF Processing Information

Process Steps

- Pretreatment Step
 - None
 - Mechanical
 - Chemical
 - Enzymatic
- Final Fibrillation Step
 - Grinding/Refining
 - Homogenization
 - Microfluidization
 - Other

Characteristics of final CNF

- Relative Liquid Content
 - Fluid Suspension
 - Gel
 - Paste
 - Dry
- Relative Degree of Dispersion
 - Individual Fibrils
 - Entangled Fibrils

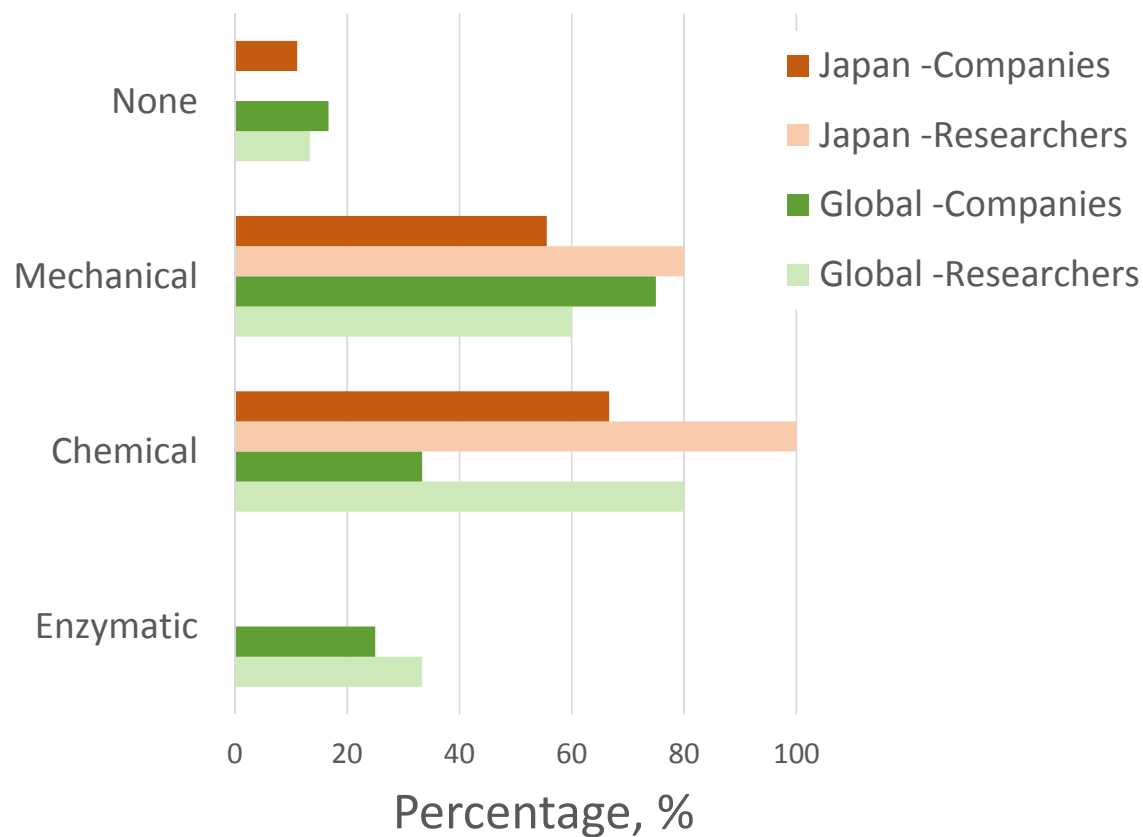
Pretreatment Step

Key Points

- Pretreatments overwhelmingly used
- Mechanical & Chemical
 - Used the most
 - Japan & Global
 - Companies & Researchers
- Chemical
 - Used more in Japan
- Enzymatic
 - Not used in Japan

Response:

- | | |
|------------------------|----|
| • Japan – Companies | 9 |
| • Japan – Researchers | 5 |
| • Global – Companies | 12 |
| • Global – Researchers | 15 |



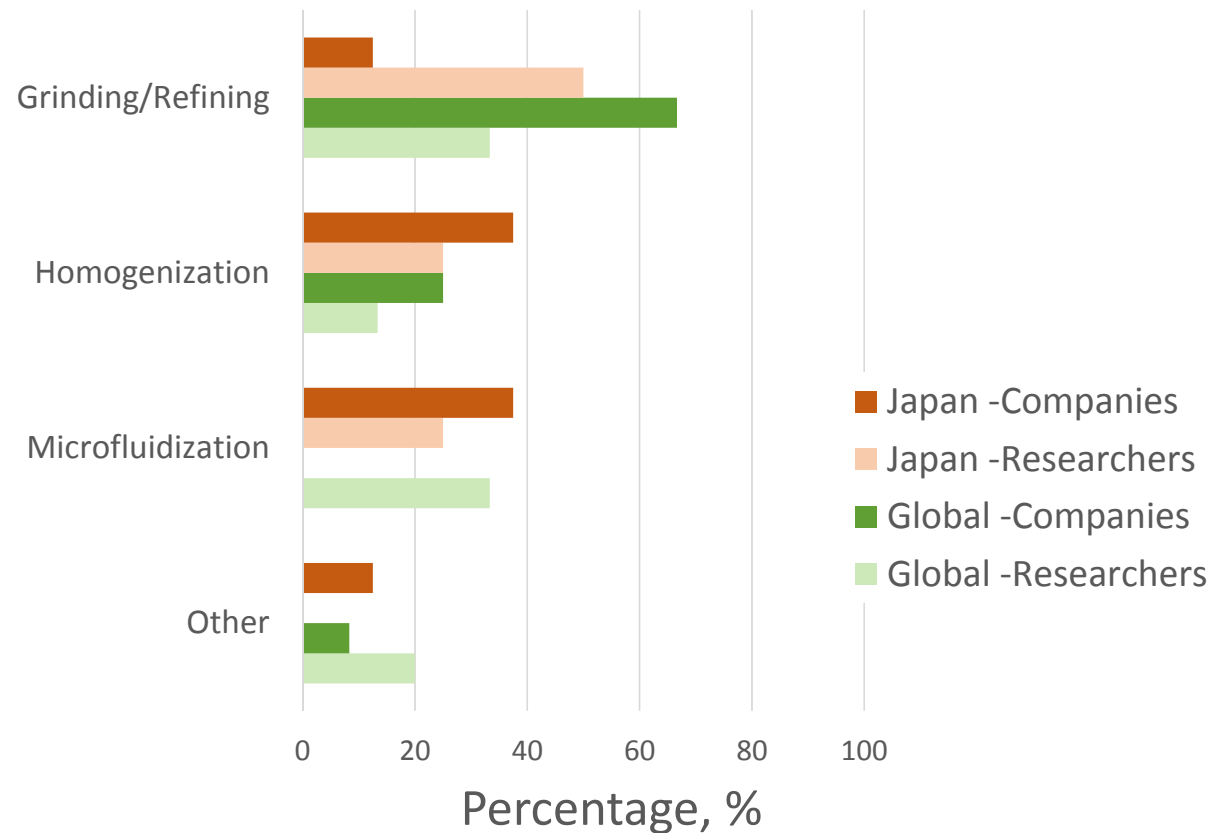
Final Fibrillation Step

Key Points

- Japan Companies
 - Homogenization & Microfluidization
- Global Companies
 - Grinding/Refining
- Other
 - Ultrasonication
 - High pressure aqueous counter collision
 - Kneading or twin-screw extrusion

Response:

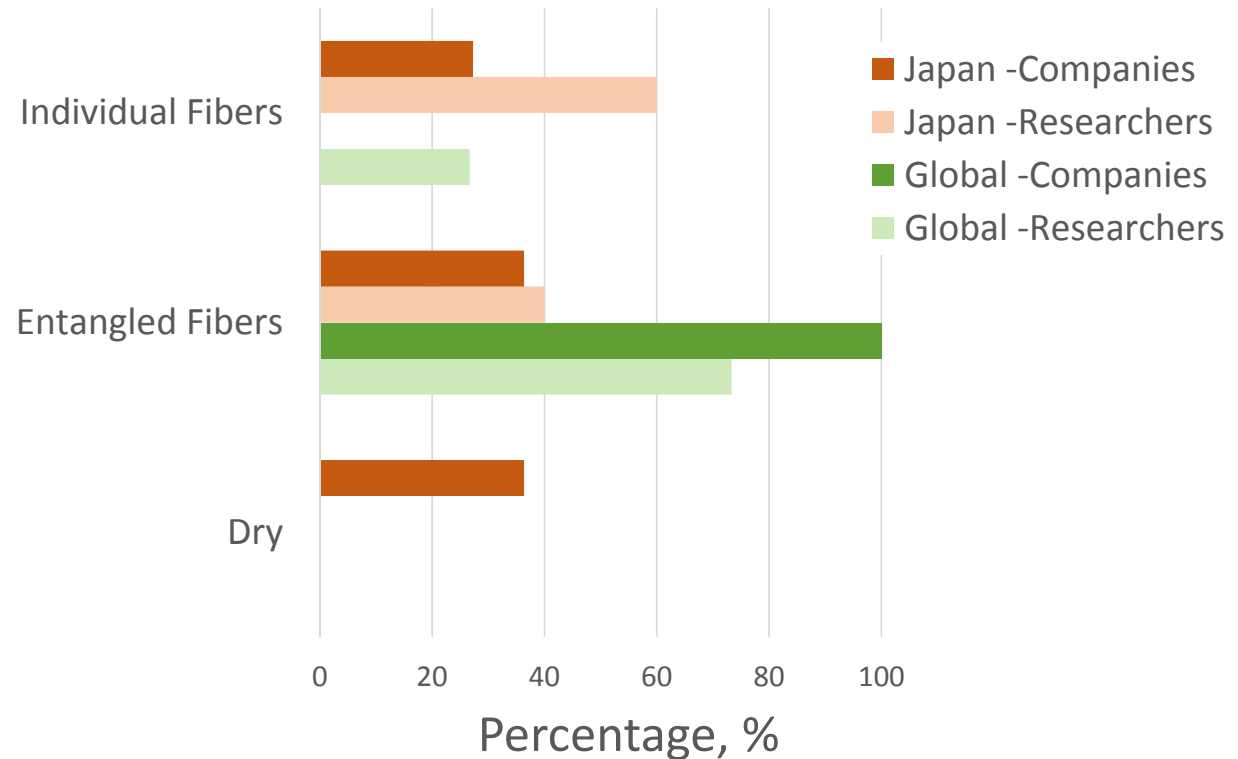
- | | |
|------------------------|----|
| • Japan – Companies | 8 |
| • Japan – Researchers | 4 |
| • Global – Companies | 12 |
| • Global – Researchers | 15 |



Relative Degree of Dispersion

Key Points

- Japan Companies
 - Individual & Entangled Fibers
- Global Companies
 - Entangled Fibers



Response:

- | | |
|------------------------|----|
| • Japan – Companies | 11 |
| • Japan – Researchers | 5 |
| • Global – Companies | 12 |
| • Global – Researchers | 15 |

C. Particle Measurement

Standardization needed for:

- Safety/Regulatory
- Product specification
- Grade definition for patents
- Benchmarking
- Production control

Dimensions to Measure?

- Width
- Length
- Aspect ratio
- Hydrodynamic Radius
- Other

Other – 10 responses total

- Surface area
- Degree of fibrillation
- Entanglement degree
- Aggregation and shape

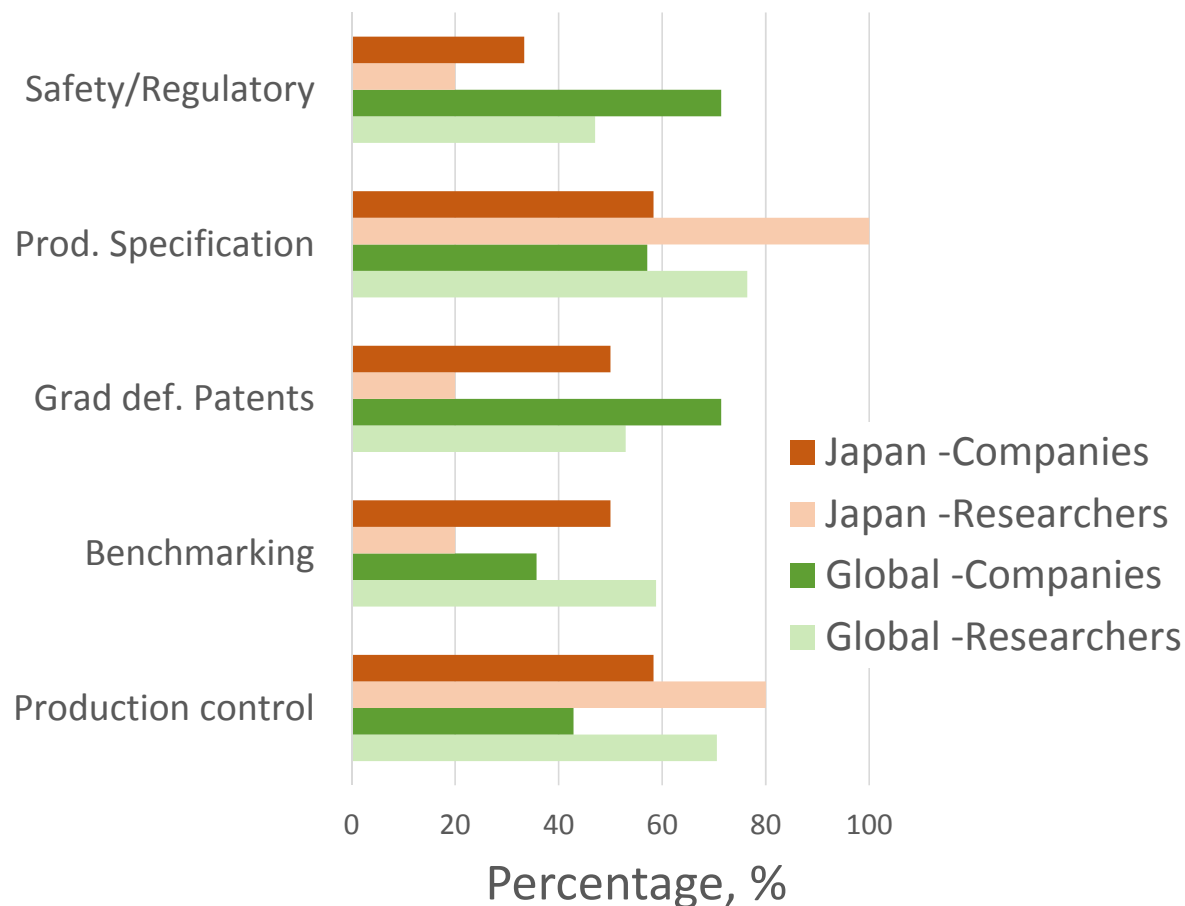
Particle Size Standards Needs.... [Now]

Key Points

- Japan Companies
 - Product Specification
 - Production Control
- Global Companies
 - Safety/Regulatory
 - Grade Definition for Patents

Response:

- | | |
|------------------------|----|
| • Japan – Companies | 12 |
| • Japan – Researchers | 5 |
| • Global – Companies | 14 |
| • Global – Researchers | 17 |



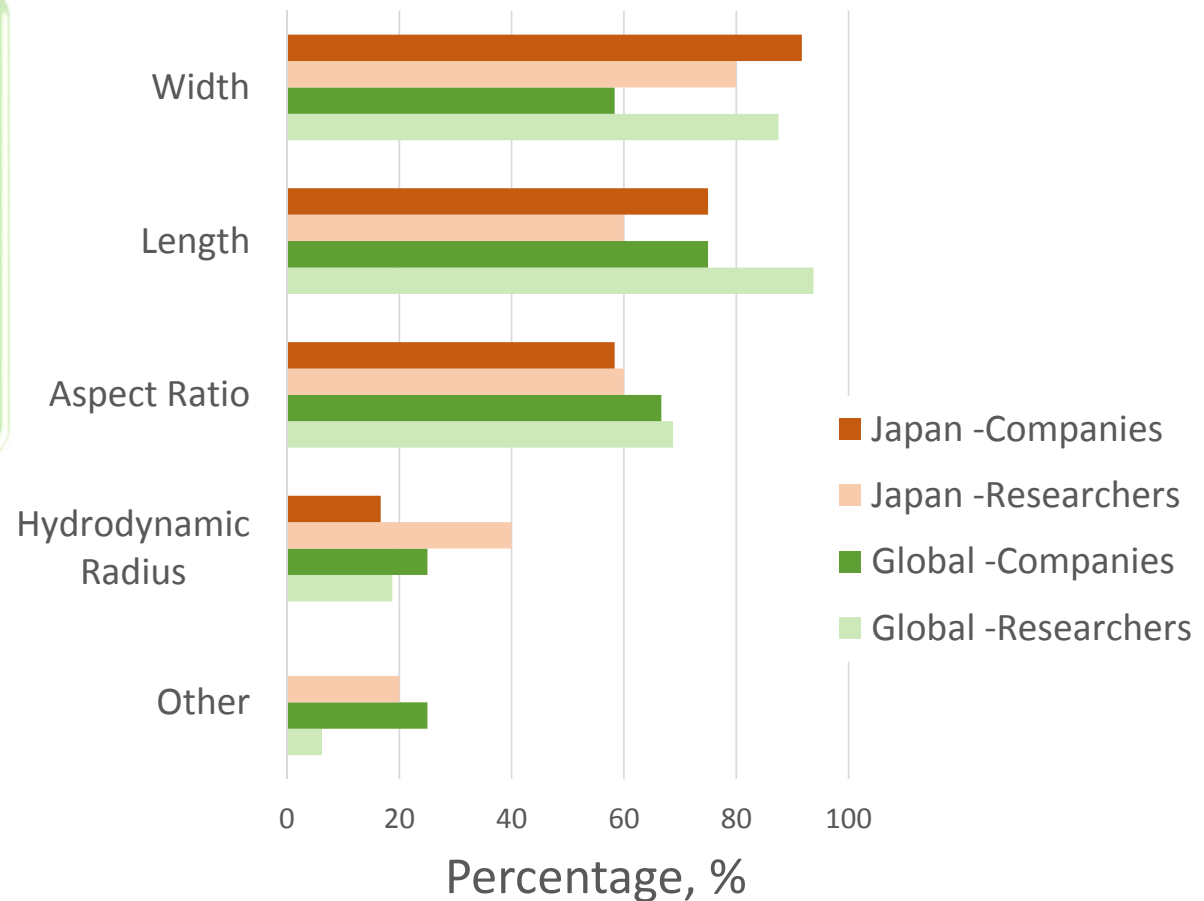
Measurements for Product Specifications

Key Points

- Width & Length are high priority
- Japan Companies
 - Width > Length > Aspect Ratio
- Global Companies
 - Length > Aspect Ratio > Width
- Hydrodynamic Radius is low priority

Response:

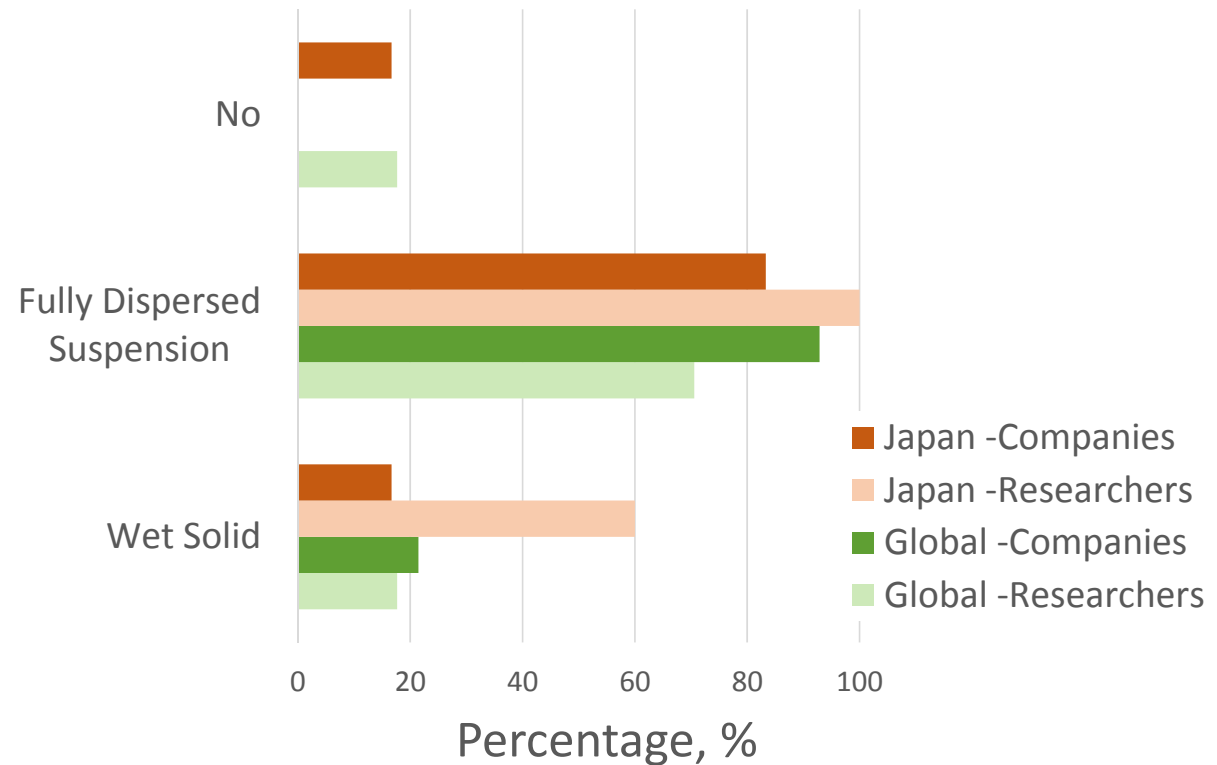
- | | |
|------------------------|----|
| • Japan – Companies | 12 |
| • Japan – Researchers | 5 |
| • Global – Companies | 12 |
| • Global – Researchers | 16 |



Measurements in Wet State?

Key Points

- Dispersed suspension is priority



Response:

- | | |
|------------------------|----|
| • Japan – Companies | 12 |
| • Japan – Researchers | 5 |
| • Global – Companies | 14 |
| • Global – Researchers | 17 |

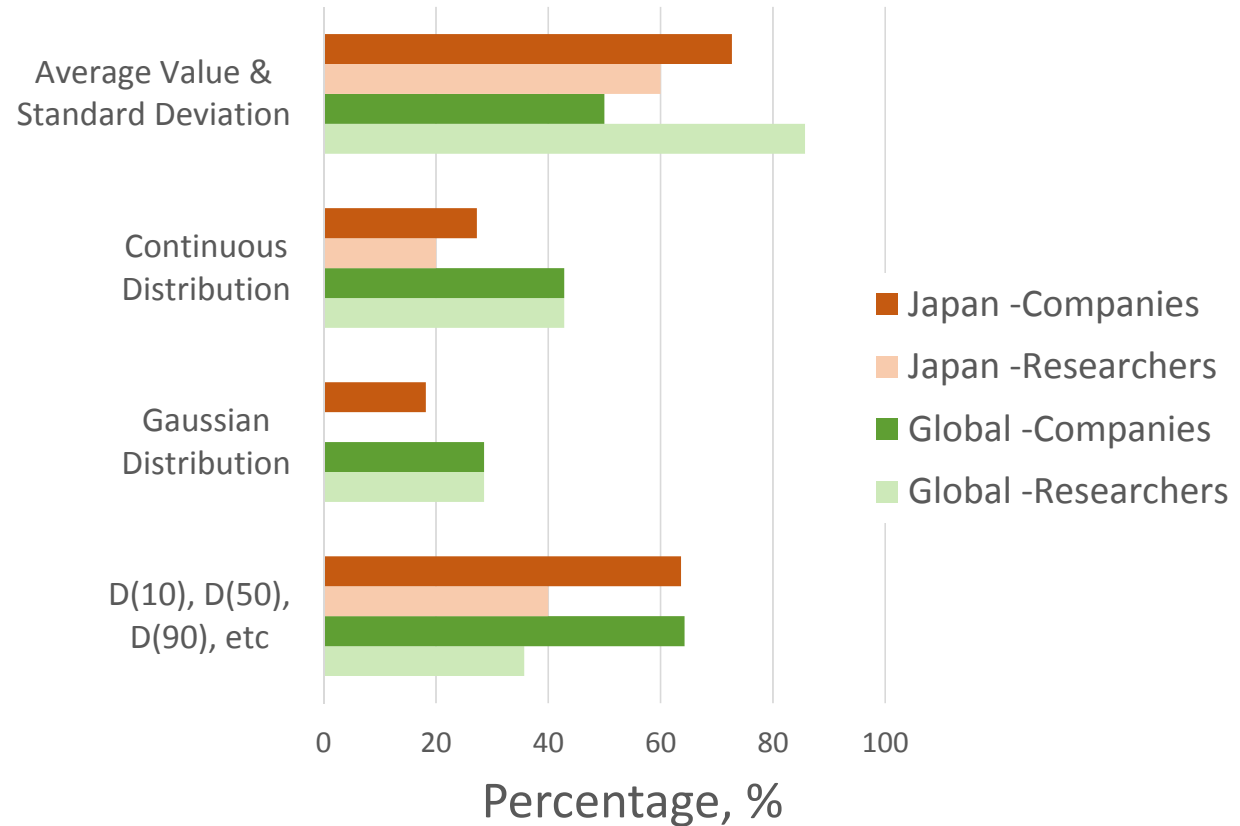
Information Needed from Size Distribution

Key Points

- Most Requested
 - Average and Standard Deviation
 - D(10), D(50), D(90), etc.

Response:

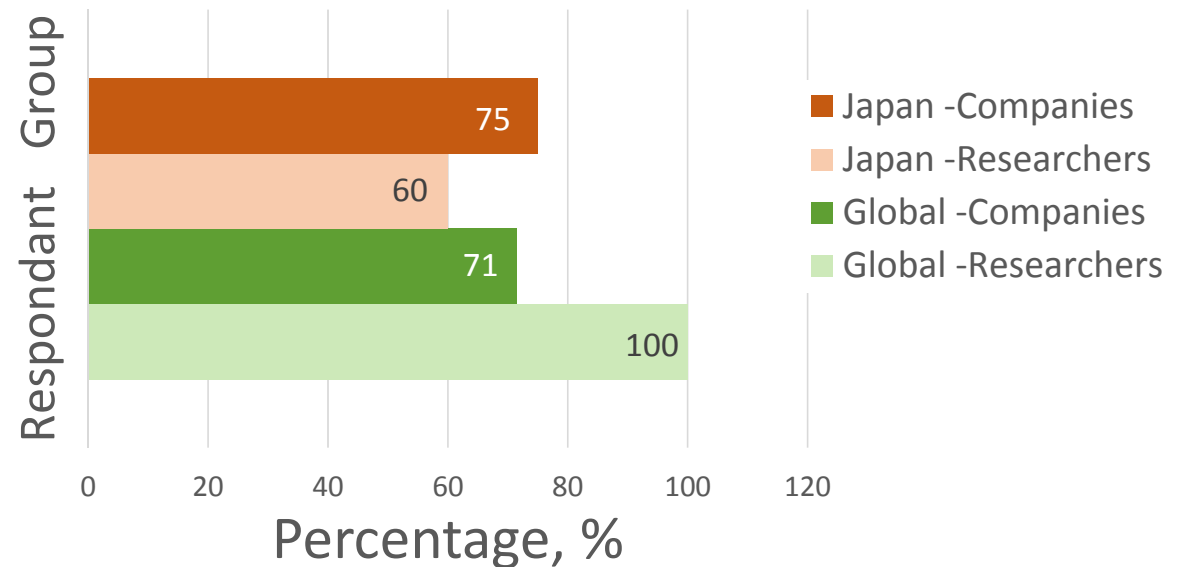
- | | |
|------------------------|----|
| • Japan – Companies | 11 |
| • Japan – Researchers | 5 |
| • Global – Companies | 14 |
| • Global – Researchers | 14 |



Who is measuring particle size?

Key Points

- Majority measure CNF size
- 75% of companies
- Japan vs. Global
 - Companies similar
 - Researchers different



Response:

- | | |
|------------------------|----|
| • Japan – Companies | 12 |
| • Japan – Researchers | 5 |
| • Global – Companies | 14 |
| • Global – Researchers | 17 |

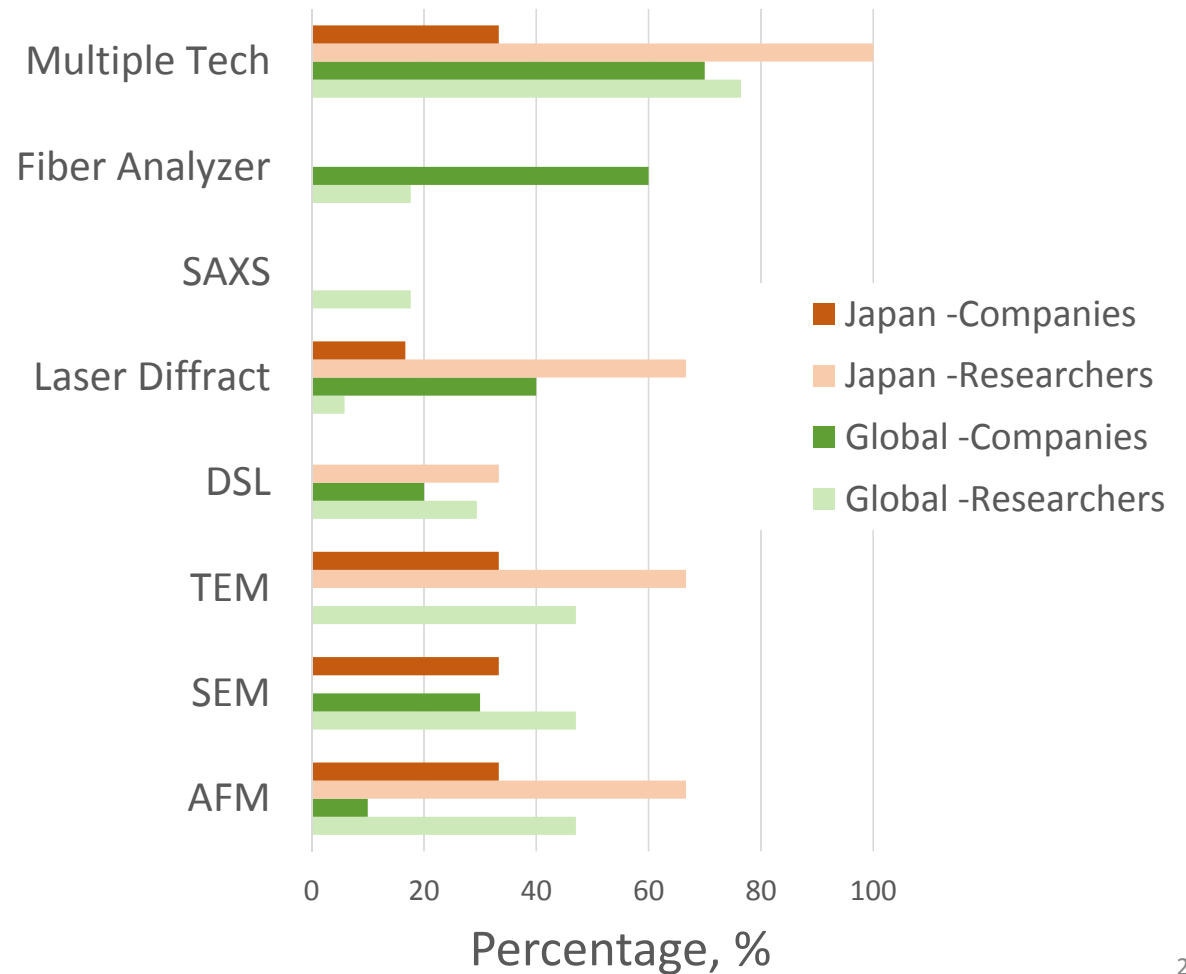
Particle Size Measurement Techniques Used

Key Points

- Most use multiple techniques
- Japan Companies
 - AFM, TEM, SEM,
- Global Companies
 - Fiber Analyzer, Laser Diffract, SEM
- Japan $\neq$ Global
 - Difference in particle type
- Companies $\neq$ Researchers
 - Differences in time, cost, skill

Response:

- | | |
|-----------------------|----|
| • Japan – Companies | 6 |
| • Japan – Researchers | 3 |
| • Global – Companies | 10 |
| • Global – Research | 17 |



Summary of Key Findings

What to measure:

- Width & Length -Primary interest
 - Japan & Global
 - Companies & Researchers
- Aspect Ratio -Secondary interest
- Hydrodynamic radius -Low interest

Comment on “Typical” CNF Materials:

- They do not have a well-defined length or width
- They contain clusters of partially-separated fibrils that can resemble frayed pieces of a string.
- Thus length and width will have little meaning
- Hydrodynamic radius may or may not be useful

Summary of Key Findings

How to report

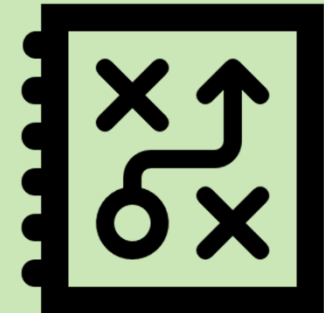
- | | |
|---|---------------------|
| • Average values and standard deviation | -Primary interest |
| • Japan & Global | |
| • Companies & Researchers | |
| • Percentiles (D(10), D(50), D(90), etc.) | -Secondary interest |
| • Japan & Global Companies | |
| • Distributions (Gaussian or continuous) | -Low interest |
| • Less popular in Japan than Global | |
| • Perhaps because Japan has more uniform material | |

Comment on “Typical” CNF Materials:

- Average and std. deviation are not particularly useful
- Distributions are useful for comparisons, but hard to convey precisely
- May be beneficial to report the whole distribution as defined by the technique being used.

Path Forward

- Complete survey analysis
 - Prepare and publish final report
 - CNF Particle Size Measurement Workshop
 - Create CNF Particle Size Standards Development Road Map
 - Techniques and methods
 - Suitability of ISO/TC 6 WGs
 - Suitability of ISO/TC 229 WGs
-] To undertake the work





Thank you!

ISO/TC 6/TG 1 Contact: Robert Moon
robert.j.moon@usda.gov

TAPPI Nano 2021 Virtual Conference
15-16 June 2021

