AVEKA Group

PARTICLE PROCESSING AND THE VALUE OF CHARACTERIZATION

DECEMBER 12,2018

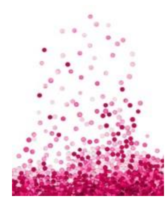
PARTICLE PROCESSING SERVICES

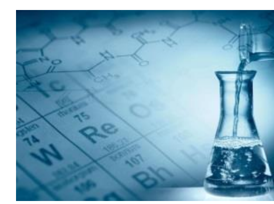
TOLL MANUFACTURING

RESEARCH & DEVELOPMENT

INNOVATIVE SOLUTIONS







PRESENTED BY: WILLIE HENDRICKSON, CEO & FOUNDER

Presentation Outline

- Overview of AVEKA
- Reasons for Characterization
- Types of Characterization Methods to Consider
- Examples of Characterization Challenges and Some Solutions
- Conclusions

AVEKA Group Overview

- Particle technology company focused on contract manufacturing
- Spin-off of 3M in 1994
- Comprised of 5 separate companies
- ISO certifications / food-grade certifications
- Currently 290 employees

ISO 9001:2015

FDA APPROVED

Food Safety System Certification 22000

NSF ISR

QUALITY ASSURANCE INTERNATIONAL CERTIFIED ORGANIC

AVEKA's Vision

be the recognized leader in
innovative manufacturing solutions
for particle technology

AVEKA's Mission

be the leader in **particle processing**
by providing our customers with custom solutions,
quality manufacturing and **excellent customer service**

The AVEKA Group

AVEKA Inc

- 75 people
- Corporate Headquarters
- R&D, Manufacturing, Specialty Process Suites

AVEKA Manufacturing

- 96 people – Fredericksburg, Iowa
- Large scale manufacturing
- Spray Drying, Hammer Milling, Fluid Bed Drying, Tumble Coating, Agglomeration

Cresco Food Technologies

- 50 people – Cresco, Iowa
- Food Processing
- Spray Drying, Prilling, Drum Drying, Extraction, Wet Blending

AVEKA Nutra Processing

- 40 people – Waukon Iowa
- Value Added Food Processing
- Spray Drying, Roll Drying, Microfiltration/Nanofiltration, Specialty Separations

AVEKA CCE Technologies

- 15 People – Cottage Grove, Minnesota
- Industrial Materials, Abrasives, Ceramics, Minerals
- Jet Milling and Classification

Particle Characterization

Particle size analysis

- Particles 1 nm to 2+ mm
- Particle size distribution (PSD)
- Sonic sieving
- Rototap

Imaging

- Optical microscopy
- Scanning electron microscopy (SEM)

Surface area analysis

True density analysis

- Helium pycnometry

Formulation analysis

- High performance liquid chromatography (HPLC)
- Thermogravimetric analysis (TGA)
- Spectrophotometer
- Differential scanning calorimetry (DSC)

Flow characteristics

- Freeman FT4
- Zeta potential analysis (ZP)
- Rheological analysis
- Moisture and solids analysis (MSA)
- Karl Fisher

Reasons for Characterization

- Scientific Curiosity
- IP Development and Protection
- Process Control/Understanding
- Product Control
- Quality Control
- Impurity Analysis

Characterization Methods

- Visual Inspection (color, flow, size, uniformity, etc.)
- Mass Balance Measurements
- Optical Microscopy
- Particle Size/Shape
- Particle Flow
- Chemical Characterization
- Surface Area
- Electrical Characteristics

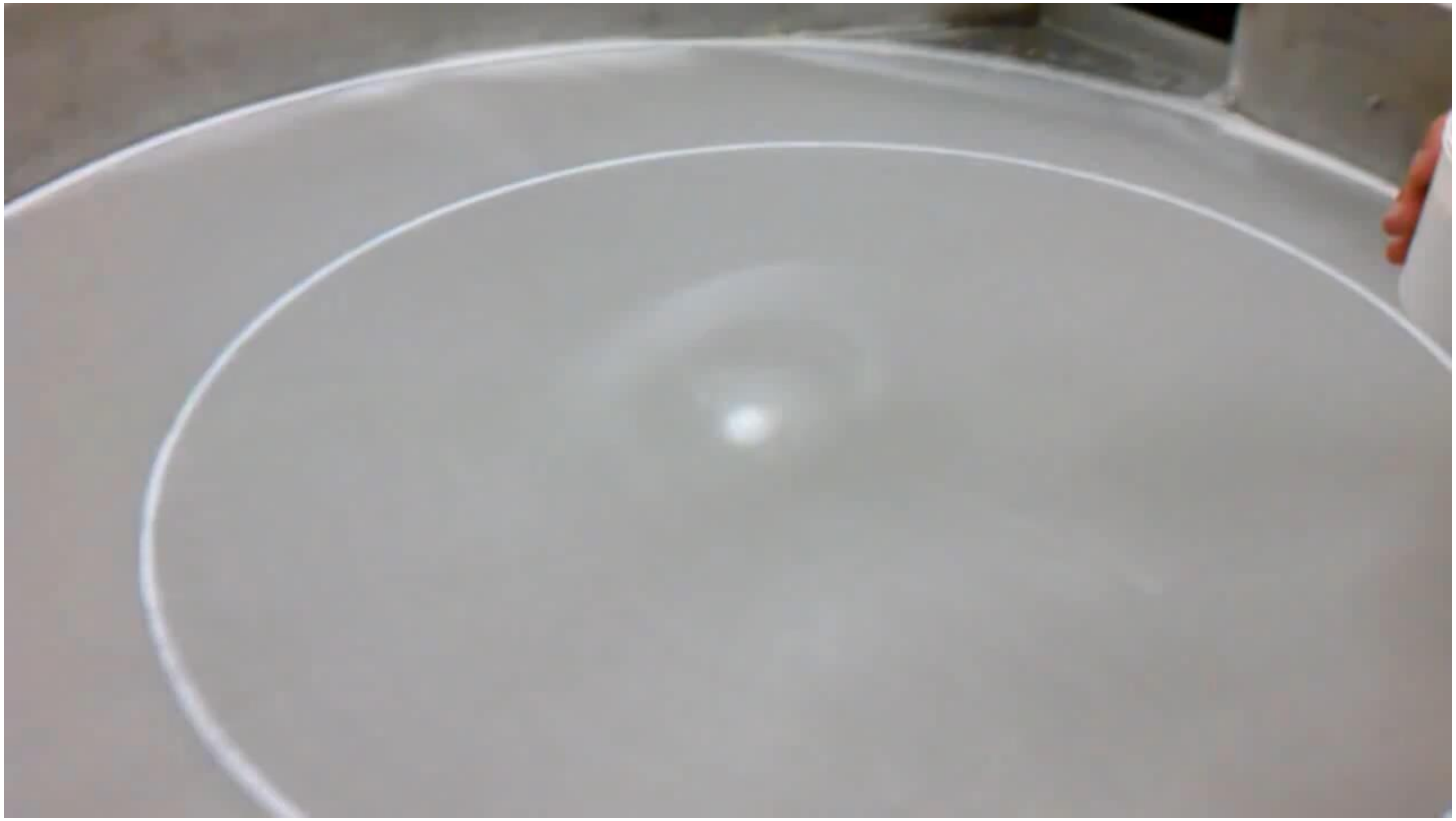
Classification by Screening

Challenge: Rapid and efficient screening of powders less than 200 microns

Screening at 74 µm of encapsulated fragrance particles using a 30 inch Screener

Rate (lbs./hr.)	Ultrasonics	Overs (%)	Product (%)
163	no	56	44
159	yes	30	70

Ultrasonic Screening



Quality Control

Process:

- Crushing and ball milling ceramic blocks
- Followed by screening

Specifications (microns)

- $d_{10} < 1.7$
- $d_{50} = 4\text{-}15$
- $d_{90} = 15\text{-}40$

Ceramic Particle Size Distribution

HORIBA LA-930 for Windows(TM) [WET(LA-930)] Ver.3.45
LA-930 system for Windows

Aveka Characterization Lab
Paul Verbanac, Lab Manager
2045 Wooddale Drive
Woodbury, MN 55125
Phone: (651)730-1729

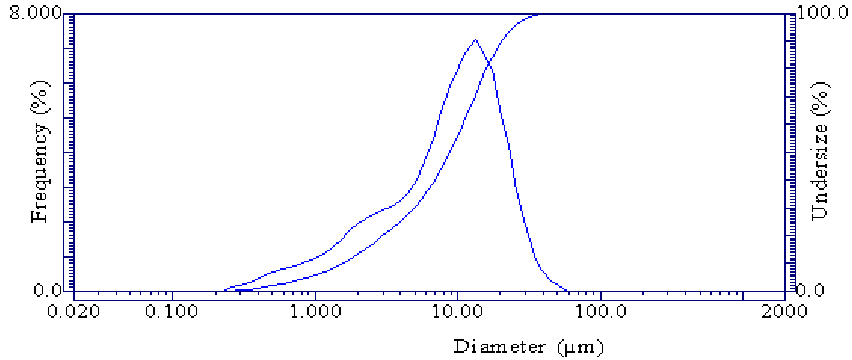
Filename :FinesBefore
ID# :200604170736086
Sample Name :Before Screening
Material :Ball Milled Fine Cordierite
Source :
Lot Number :M06409

Form of Distribution :Standard
Distribution Base :Volume
Sampling Times(:10
S.P. Area : 16460(cm² /cm³)
Median : 8.8305(μm)
Mean : 10.1737(μm)
Mode : 12.3755(μm)
Span : 2.1489

Circulation Speed :3
Ultra sonic :OFF
Laser T% : 42.4(%)
Lamp T% : 41.4(%)
Calc. Level :30
R.R.Index :116a000i
Variance : 59.740(μm²)
S.D. : 7.7292(μm)
CV : 75.9723
Geo. Mean : 6.9494(μm)
Chi-2 : 0.037355

% on Diameter
:(1)5.000 (%)- 0.9042(μm)
(2)10.00 (%)- 1.5711(μm)
(3)50.00 (%)- 8.8305(μm)
(4)90.00 (%)- 20.5467(μm)
(5)99.00 (%)- 34.3657(μm)

Diameter on %
:350.0 (μm)- 100.000(%)
176.0 (μm)- 100.000(%)
88.00 (μm)- 100.000(%)
44.00 (μm)- 99.803(%)
22.00 (μm)- 92.085(%)
11.00 (μm)- 60.751(%)
5.500 (μm)- 32.749(%)
1.945 (μm)- 12.877(%)



No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %	No.	Diameter	Freq. %	Under %
1	0.022	0.000	0.000	22	0.389	0.354	0.905	43	6.720	4.386	38.905	64	116.210	0.000	100.000
2	0.026	0.000	0.000	23	0.445	0.449	1.354	44	7.697	5.139	44.044	65	133.103	0.000	100.000
3	0.029	0.000	0.000	24	0.510	0.541	1.895	45	8.816	5.875	49.919	66	152.453	0.000	100.000
4	0.034	0.000	0.000	25	0.584	0.618	2.513	46	10.097	6.476	56.395	67	174.616	0.000	100.000
5	0.039	0.000	0.000	26	0.669	0.685	3.198	47	11.565	6.903	63.298	68	200.000	0.000	100.000
6	0.044	0.000	0.000	27	0.766	0.752	3.950	48	13.246	7.235	70.533	69	229.075	0.000	100.000
7	0.051	0.000	0.000	28	0.877	0.838	4.788	49	15.172	6.889	77.422	70	262.376	0.000	100.000
8	0.058	0.000	0.000	29	1.005	0.952	5.740	50	17.377	6.360	83.782	71	300.518	0.000	100.000
9	0.067	0.000	0.000	30	1.151	1.069	6.809	51	19.904	5.248	89.030	72	344.206	0.000	100.000
10	0.076	0.000	0.000	31	1.318	1.248	8.057	52	22.797	4.141	93.171	73	394.244	0.000	100.000
11	0.087	0.000	0.000	32	1.510	1.440	9.497	53	26.111	2.897	96.068	74	451.556	0.000	100.000
12	0.100	0.000	0.000	33	1.729	1.717	11.214	54	29.907	1.879	97.947	75	517.200	0.000	100.000
13	0.115	0.000	0.000	34	1.981	1.921	13.135	55	34.255	1.039	98.986	76	592.387	0.000	100.000
14	0.131	0.000	0.000	35	2.269	2.079	15.214	56	39.234	0.573	99.559	77	678.504	0.000	100.000
15	0.150	0.000	0.000	36	2.599	2.219	17.434	57	44.938	0.288	99.847	78	777.141	0.000	100.000
16	0.172	0.000	0.000	37	2.976	2.349	19.783	58	51.471	0.153	100.000	79	890.116	0.000	100.000
17	0.197	0.000	0.000	38	3.409	2.412	22.195	59	58.953	0.000	100.000	80	1019.515	0.000	100.000
18	0.226	0.000	0.000	39	3.905	2.576	24.771	60	67.523	0.000	100.000	81	1167.725	0.000	100.000
19	0.259	0.121	0.121	40	4.472	2.826	27.596	61	77.339	0.000	100.000	82	1337.481	0.000	100.000
20	0.296	0.174	0.295	41	5.122	3.202	30.798	62	88.583	0.000	100.000	83	1531.914	0.000	100.000
21	0.339	0.257	0.552	42	5.867	3.722	34.520	63	101.460	0.000	100.000	84	1754.613	0.000	100.000

Ceramic Particle Size Distribution After Screening

HORIBA LA-930 for Windows(TM) [WET(LA-930)] Ver.3.45
LA-930 system for Windows

Aveka Characterization Lab
Paul Verbanac, Lab Manager
2045 Wooddale Drive
Woodbury, MN 55125
Phone: (651)730-1729

Filename :FinesAfter
ID# :200604190818167
Sample Name :After Screening
Material :Ball Milled Fine Cordierite
Source :Corning
Lot Number :M06409

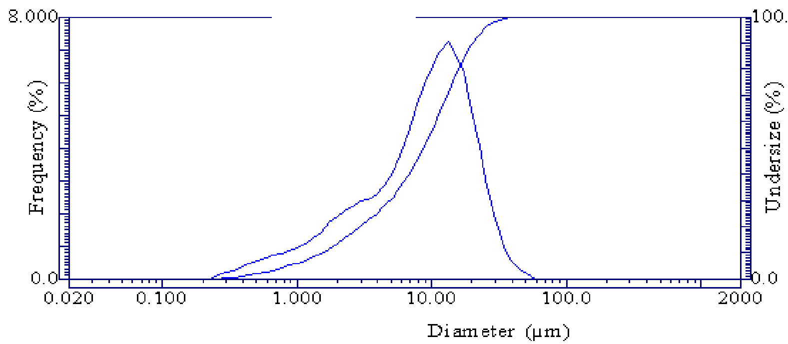
Form of Distribution :Standard
Distribution Base :Volume
Sampling Times(:10

S.P. Area : 16657(cm² /cm³)
Median : 8.7309(μm)
Mean : 10.0772(μm)
Mode : 12.3672(μm)
Span : 2.1515

Circulation Speed :3
Ultra sonic :OFF
Laser T% : 43.1(%)
Lamp T% : 41.9(%)
Calc. Level :30
R.R.Index :116a000i
Variance : 58.865(μm²)
S.D. : 7.6723(μm)
CV : 76.1358
Geo. Mean : 6.8788(μm)
Chi-2 : 0.038863

% on Diameter
(1)5.000 (%)- 0.8871(μm)
(2)10.00 (%)- 1.5545(μm)
(3)50.00 (%)- 8.7309(μm)
(4)90.00 (%)- 20.3388(μm)
(5)99.00 (%)- 34.1810(μm)

Diameter on %
350.0 (μm)- 100.000(%)
176.0 (μm)- 100.000(%)
88.00 (μm)- 100.000(%)
44.00 (μm)- 99.807(%)
22.00 (μm)- 92.334(%)
11.00 (μm)- 61.316(%)
5.500 (μm)- 33.020(%)
1.945 (μm)- 12.996(%)



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2	0.026	0.000	0.000	23	0.445	0.465	1.403	44	7.697	5.211	44.482	65	133.103	0.000	100.000
3	0.029	0.000	0.000	24	0.510	0.560	1.963	45	8.816	5.940	50.423	66	152.453	0.000	100.000
4	0.034	0.000	0.000	25	0.584	0.638	2.601	46	10.097	6.524	56.947	67	174.616	0.000	100.000
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7	0.051	0.000	0.000	28	0.877	0.850	4.922	49	15.172	6.840	77.934	70	262.376	0.000	100.000
8	0.058	0.000	0.000	29	1.005	0.960	5.881	50	17.377	6.278	84.212	71	300.518	0.000	100.000
9	0.067	0.000	0.000	30	1.151	1.072	6.953	51	19.904	5.145	89.357	72	344.206	0.000	100.000
10	0.076	0.000	0.000	31	1.318	1.246	8.200	52	22.797	4.035	93.392	73	394.244	0.000	100.000
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12	0.100	0.000	0.000	33	1.729	1.708	11.342	54	29.907	1.814	98.014	75	517.200	0.000	100.000
13	0.115	0.000	0.000	34	1.981	1.911	13.253	55	34.255	1.002	99.016	76	592.387	0.000	100.000
14	0.131	0.000	0.000	35	2.269	2.073	15.326	56	39.234	0.554	99.570	77	678.504	0.000	100.000
15	0.150	0.000	0.000	36	2.599	2.219	17.544	57	44.938	0.280	99.850	78	777.141	0.000	100.000
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20	0.296	0.180	0.304	41	5.122	3.248	31.039	62	88.583	0.000	100.000	83	1531.914	0.000	100.000
21	0.339	0.266	0.571	42	5.867	3.779	34.818	63	101.460	0.000	100.000	84	1754.613	0.000	100.000

Results of Screening

Size Distributions Exactly the Same

- Some product was usable
- Some product was not usable

Why?

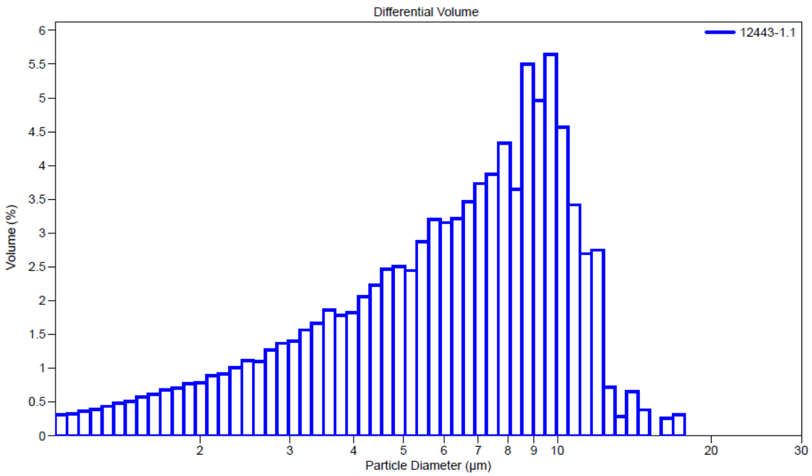
- Small quantity of unmeasured large particles

Solution

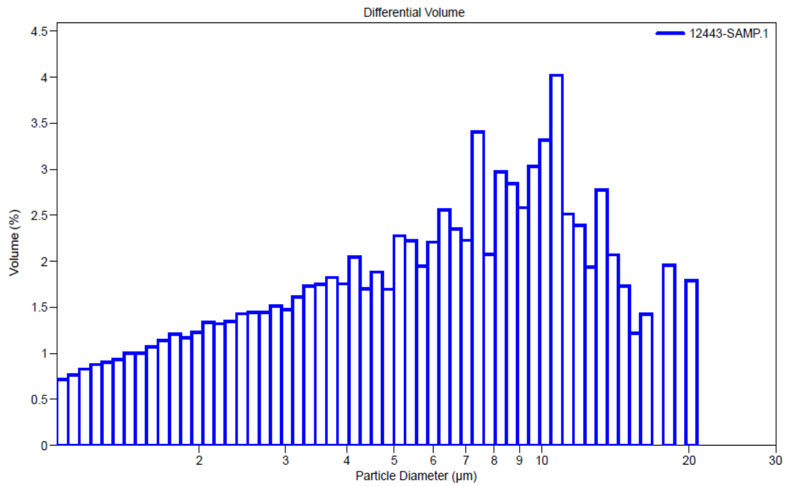
- Wet screening and microscopic evaluation

Jet Milling vs. Ball Milling of Zirconia Sand

Jet Milling



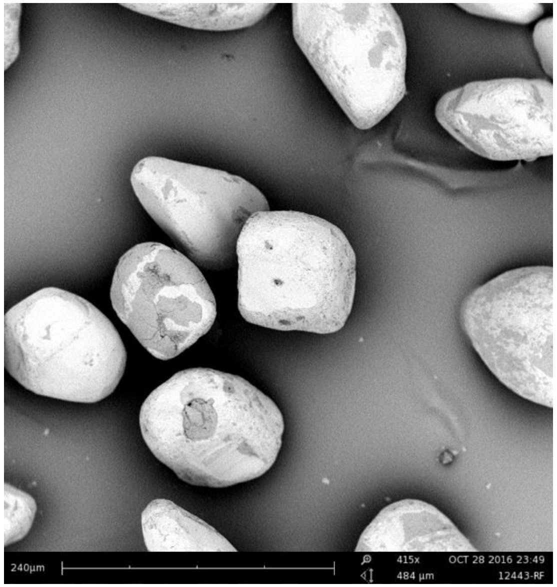
Ball Milling



Objective: Minimization of Fines

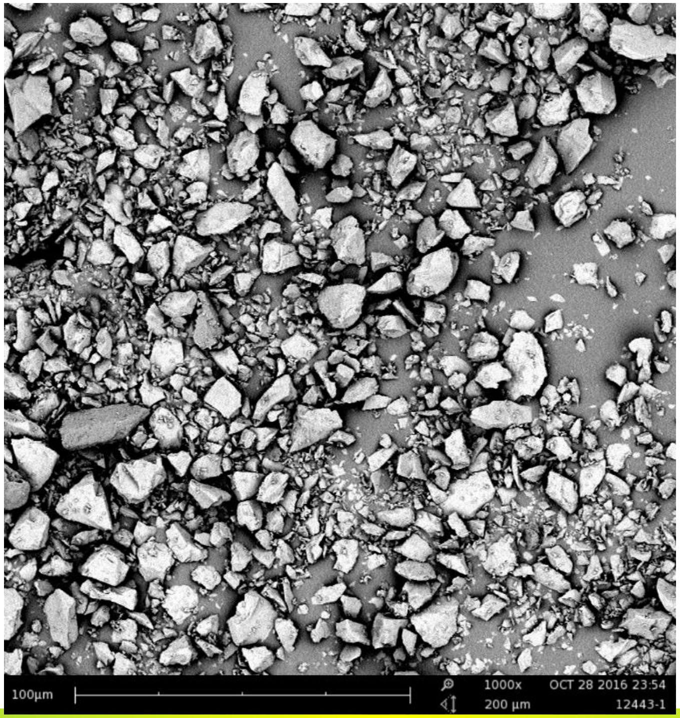
	<10%	<25%	<50%	<75%	<90%
Ball Milling	1.796 µm	3.191 µm	6.317 µm	10.25 µm	13.66 µm
Jet Milling	2.449 µm	4.120 µm	6.671 µm	9.133 µm	10.75 µm

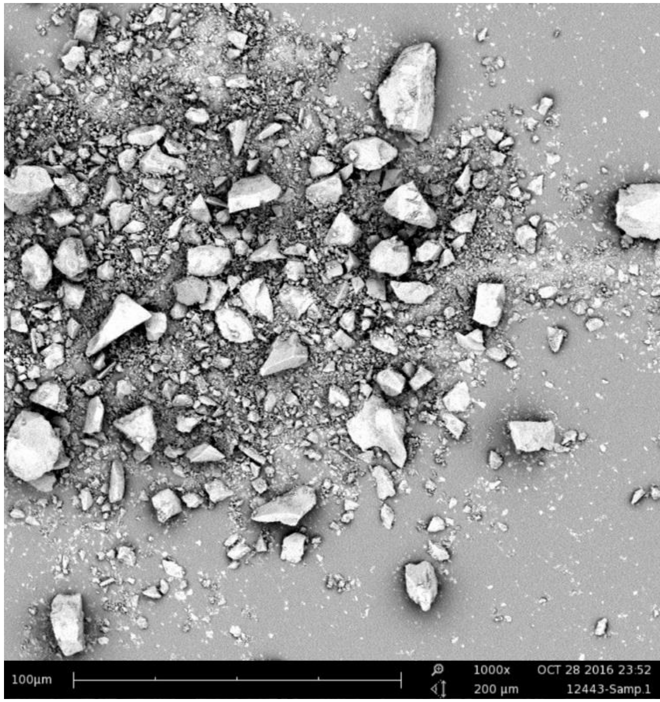
Jet Milling vs. Ball Milling of Zirconia Sand



Starting Zirconia Sand

Jet Milled Zirconia

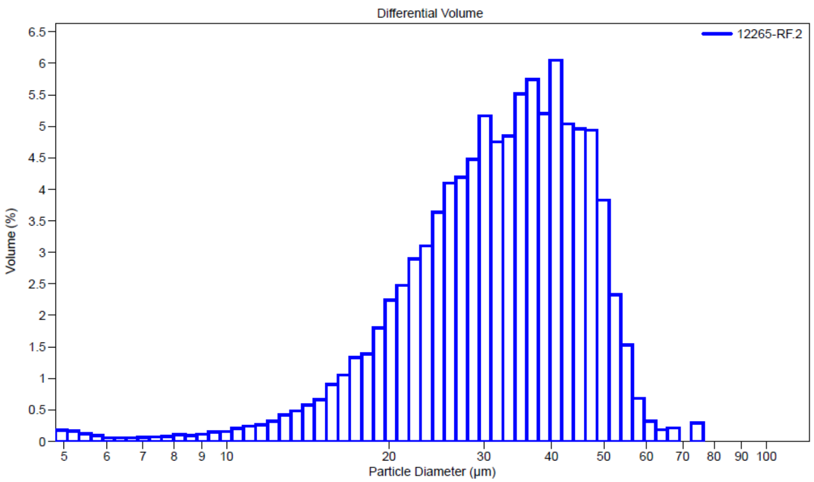




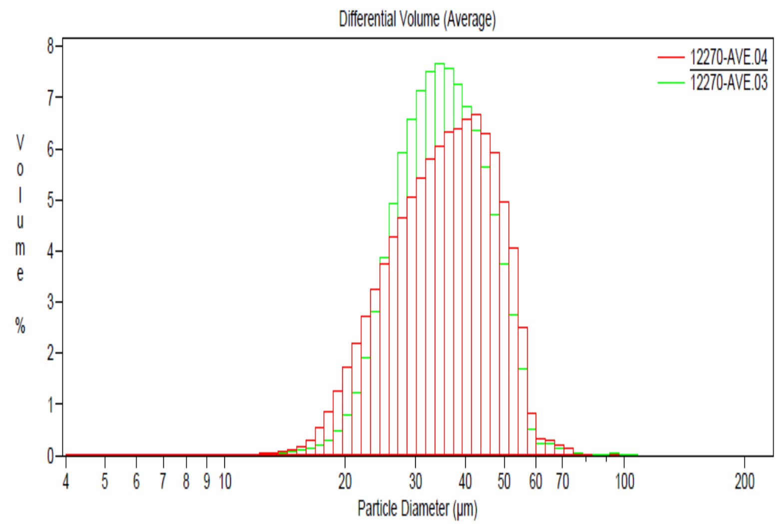
Ball Milled Zirconia

Glass Bead Classifications and Yields

Glass Beads Starting Material



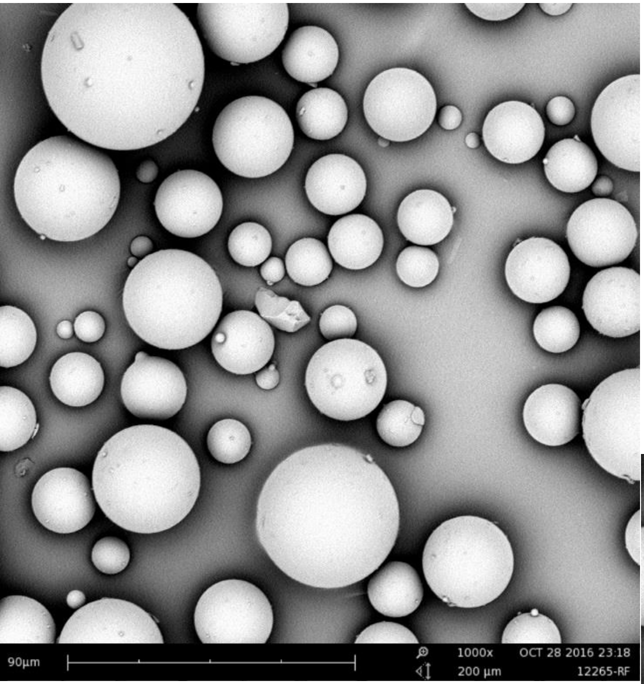
Glass Bead Classification (2 Versions)



	<10%	<25%	<50%	<75%	<90%
Starting Glass	19.01 µm	25.08 µm	33.10 µm	41.56 µm	48.29 µm
Classification (red)	23.95 µm	28.22 µm	35.82 µm	43.94 µm	50.41 µm
Classification (green)	24.95 µm	29.05 µm	34.89 µm	41.96 µm	48.47 µm

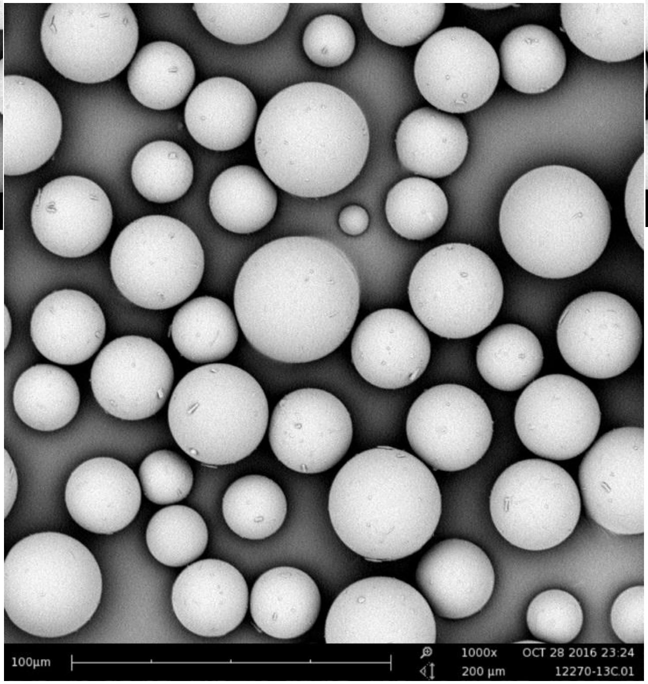
Objective: Increase yield after classification

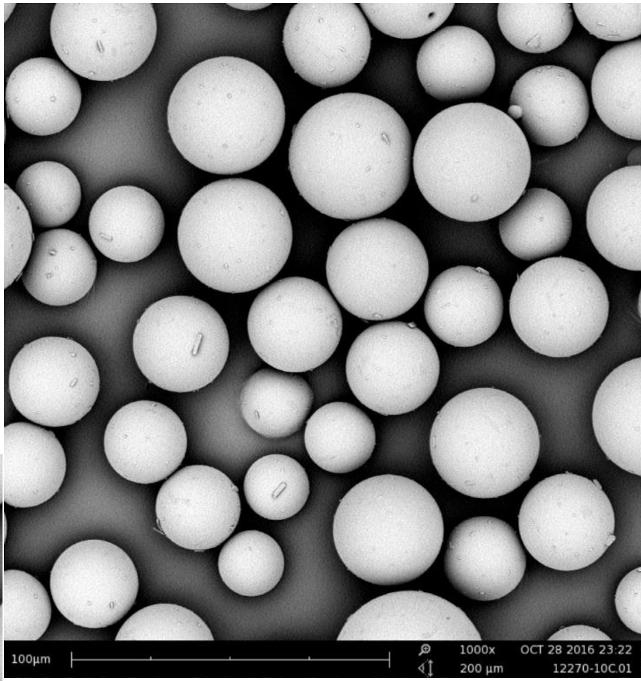
Glass Bead Classification and Yields



Starting Beads

Broad Cut (24-50 µm)
73% Yield

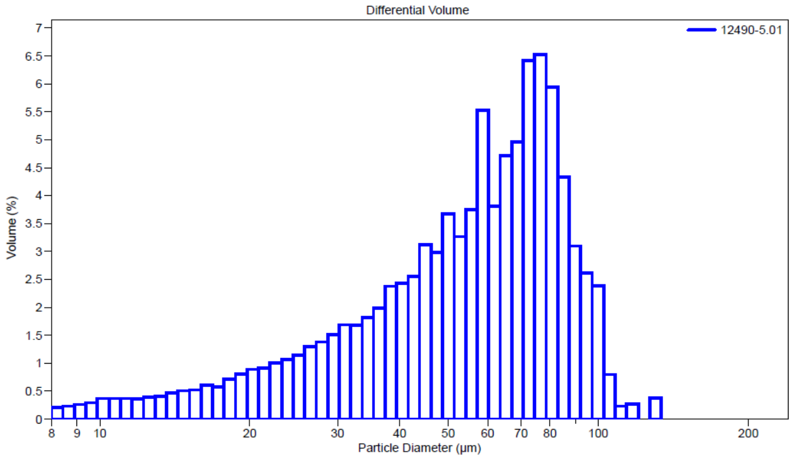


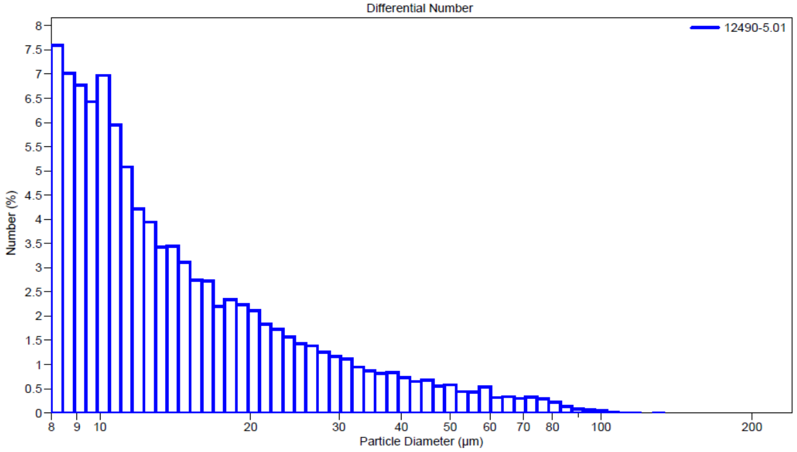


Narrow Cut (25-48 µm)
43% Yield

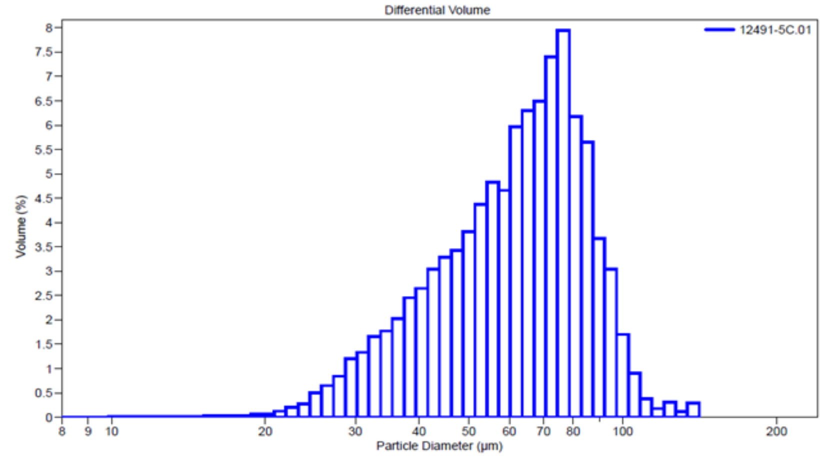
Jet Milling and Classification of Polymer

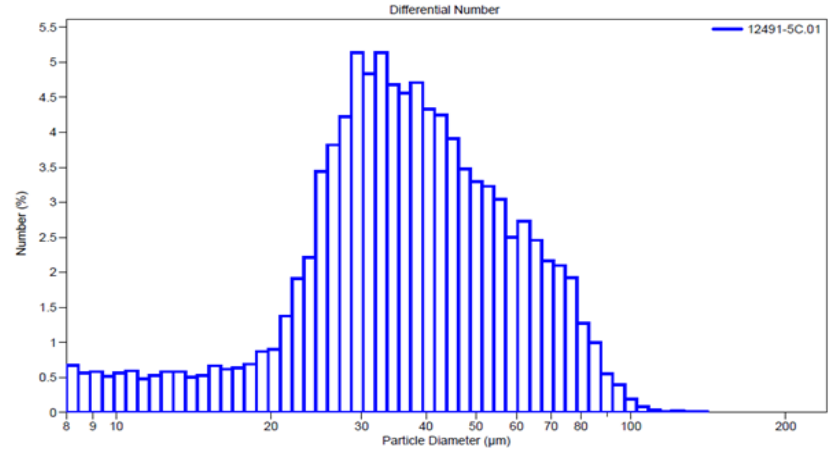
Jet Milled Polymer



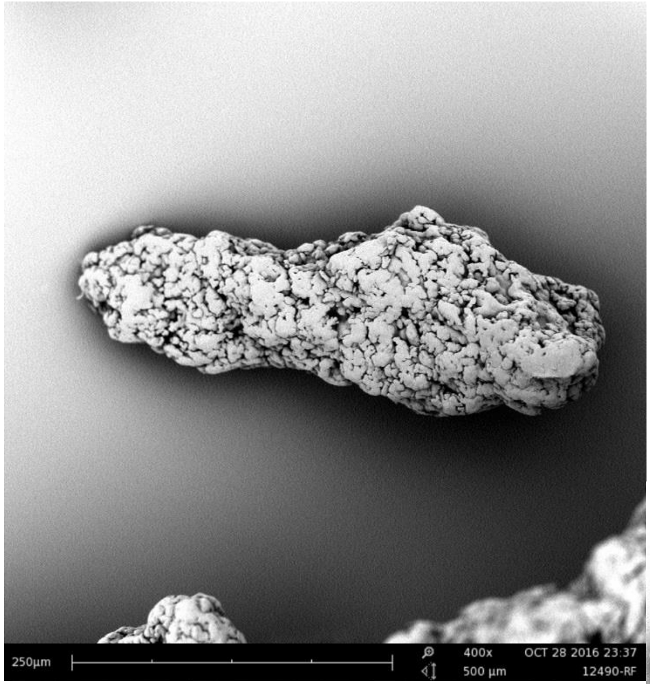


Jet Milled and Classified Polymer



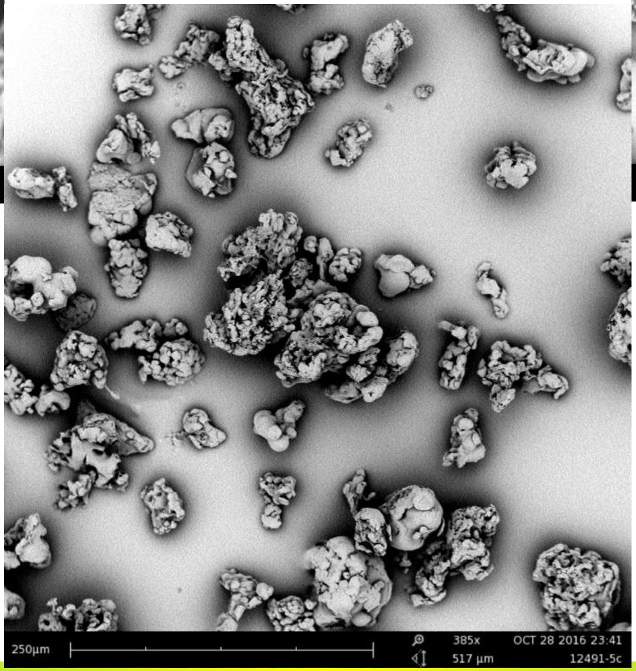


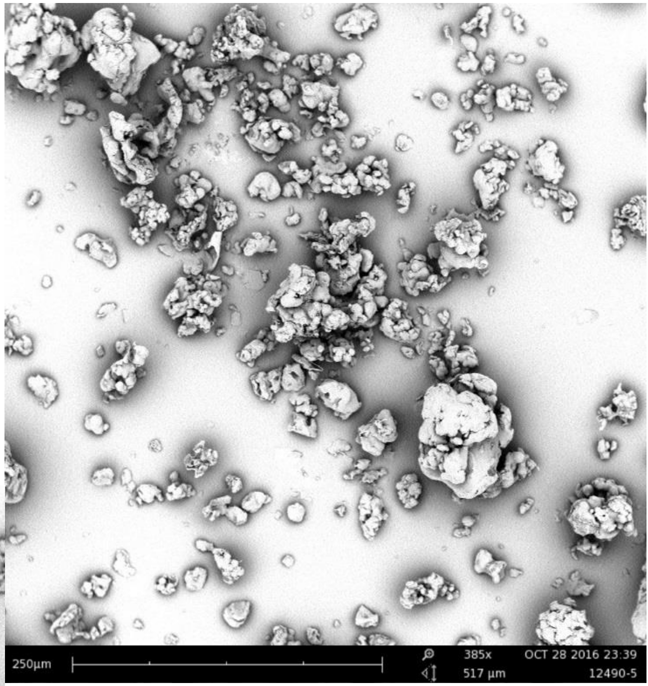
Jet Milling and Classification of Polymer



Starting Material

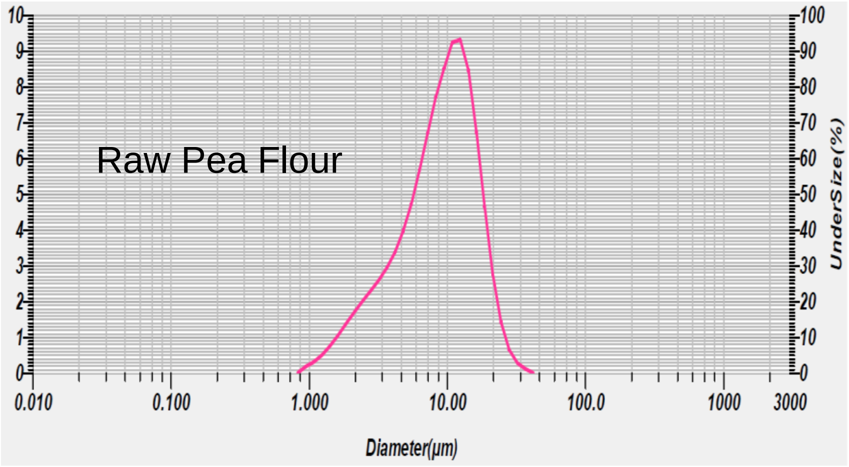
Jet Milled and
Classified Polymer

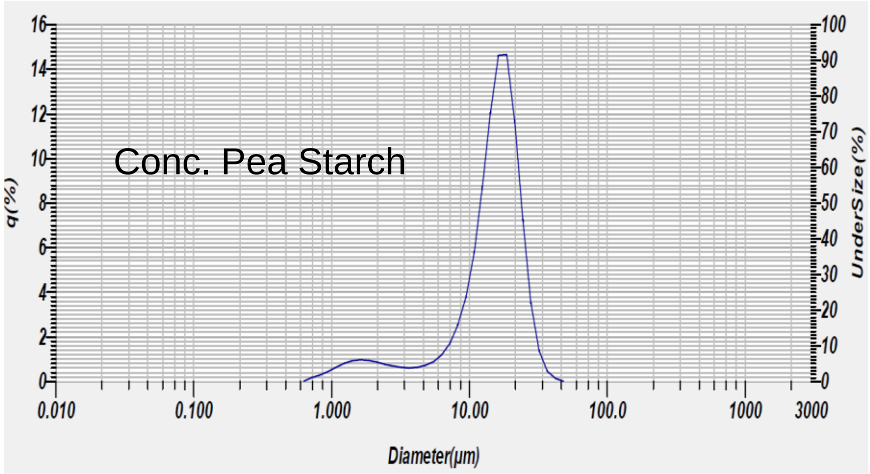


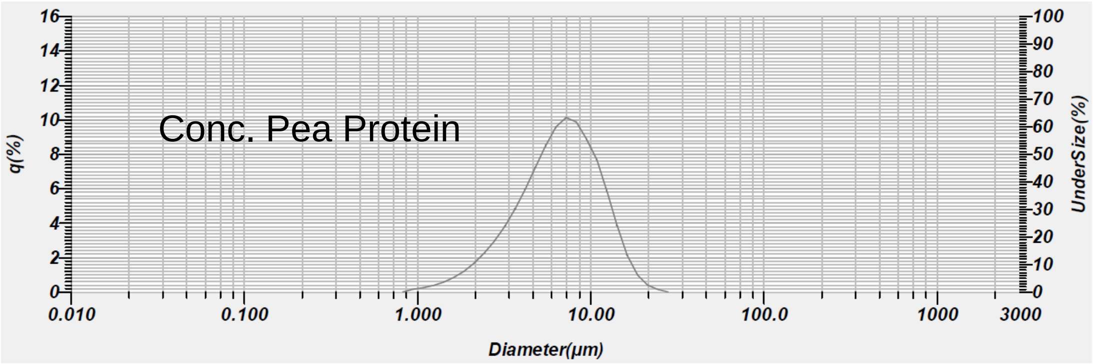


Jet Milled Polymer

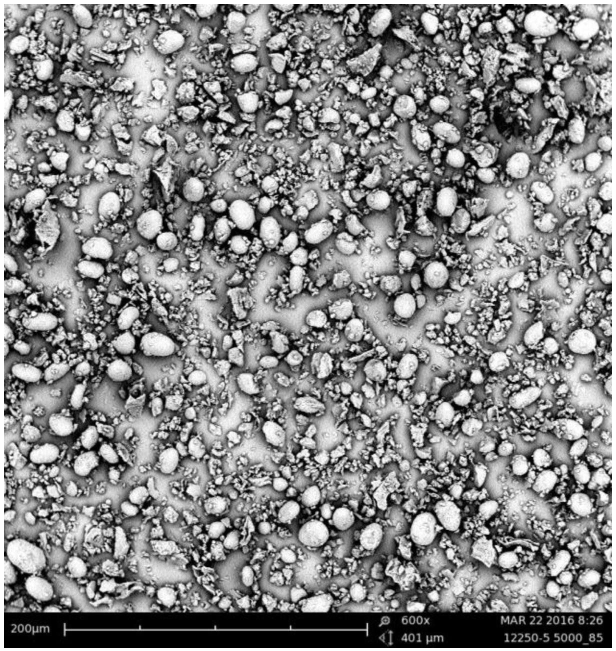
Jet Milling and Separation of Starch and Protein





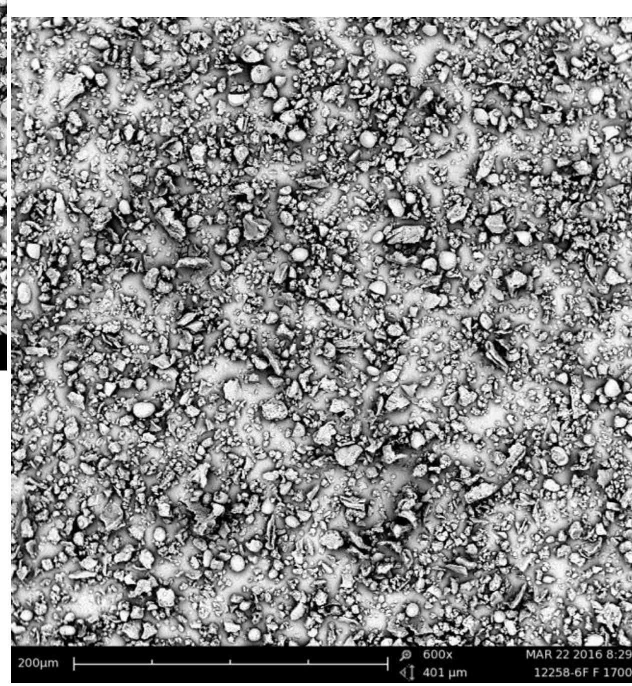


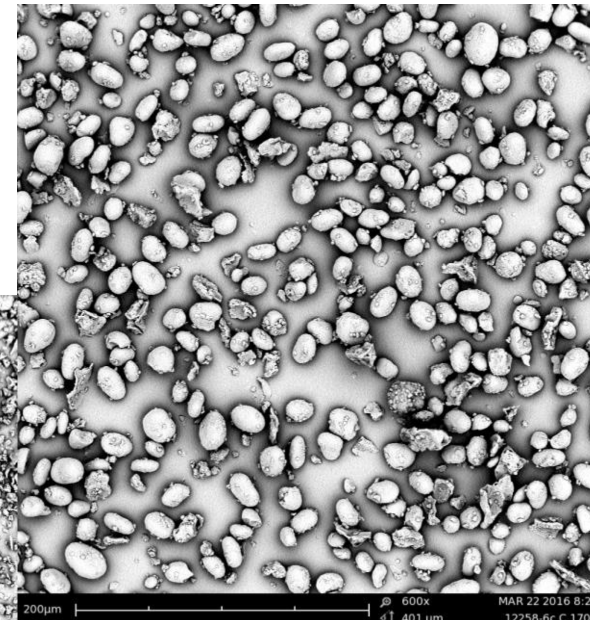
Jet Milling and Air Separation of Starch & Protein



Raw Pea Flour

Conc. Pea Protein





Conc. Pea Starch

Spheroidizing

Particle size

- remains the same

Processing Rate

- up to 20 kg/hour

Atomization Air Temp

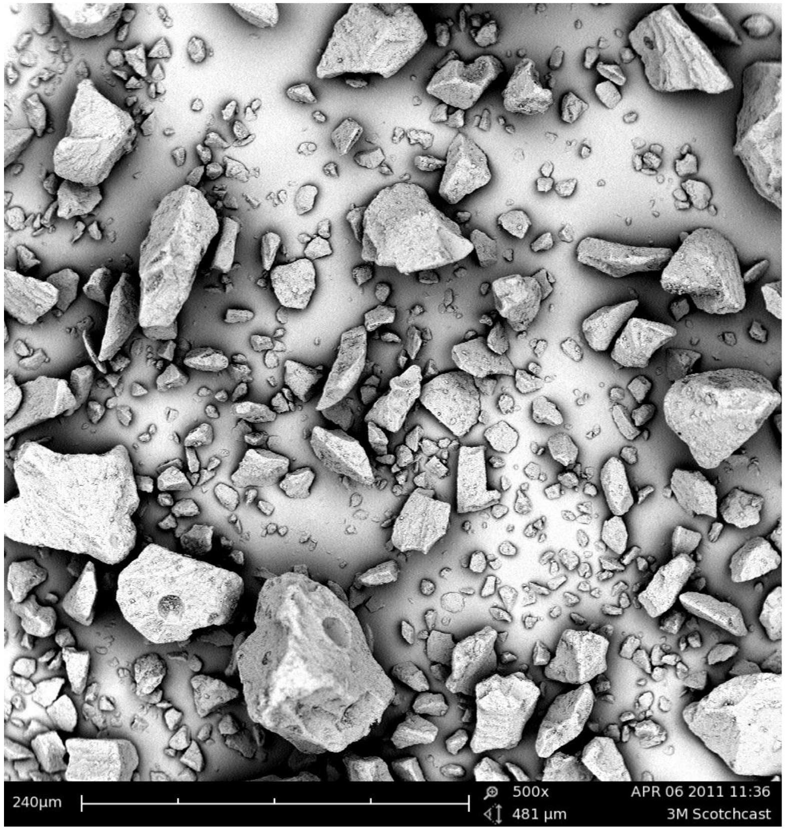
- up to 650°C

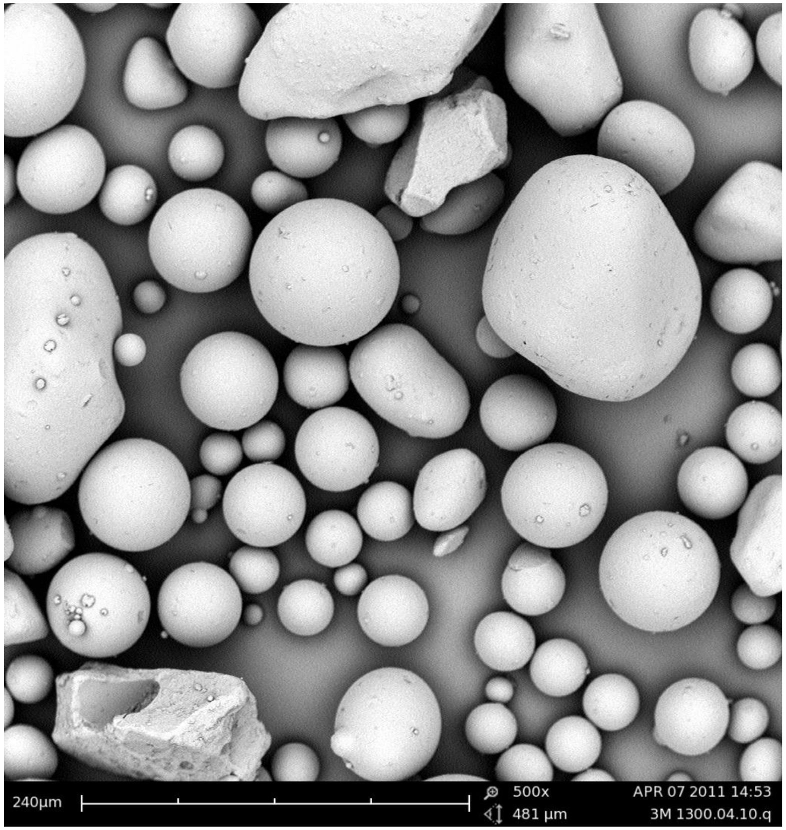
Industrial materials

Ideal Materials

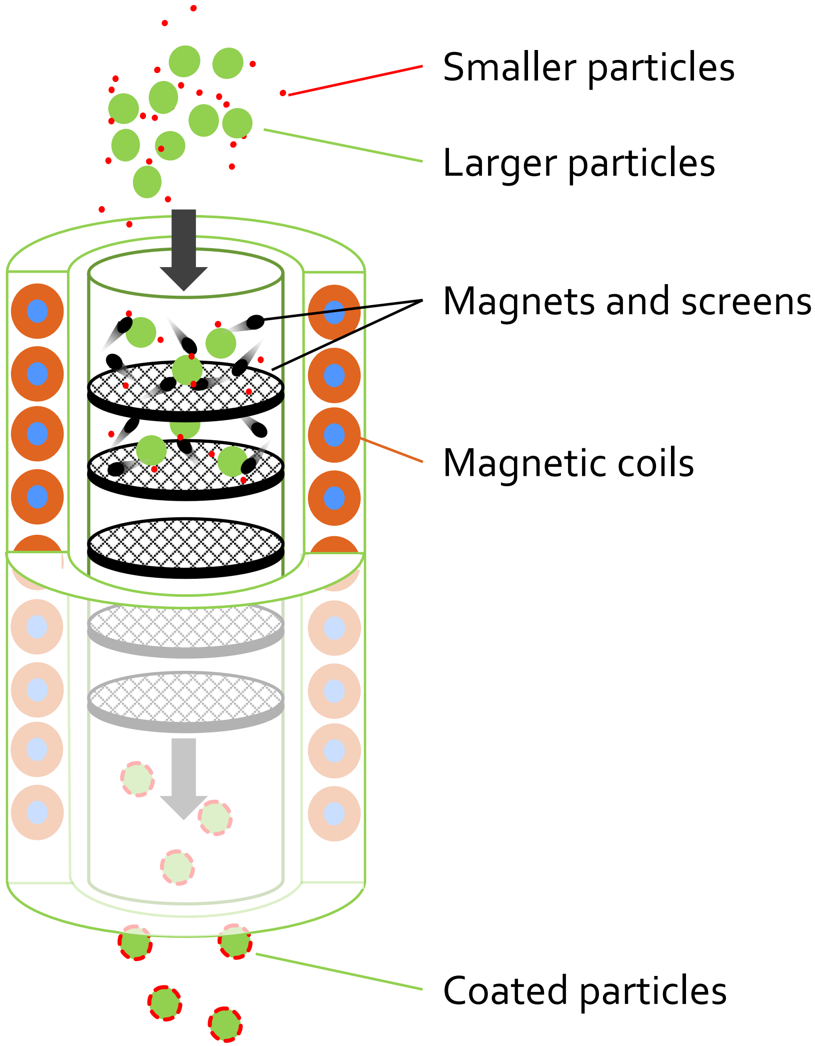
- Thermoplastics, pigments

Spheroidizing



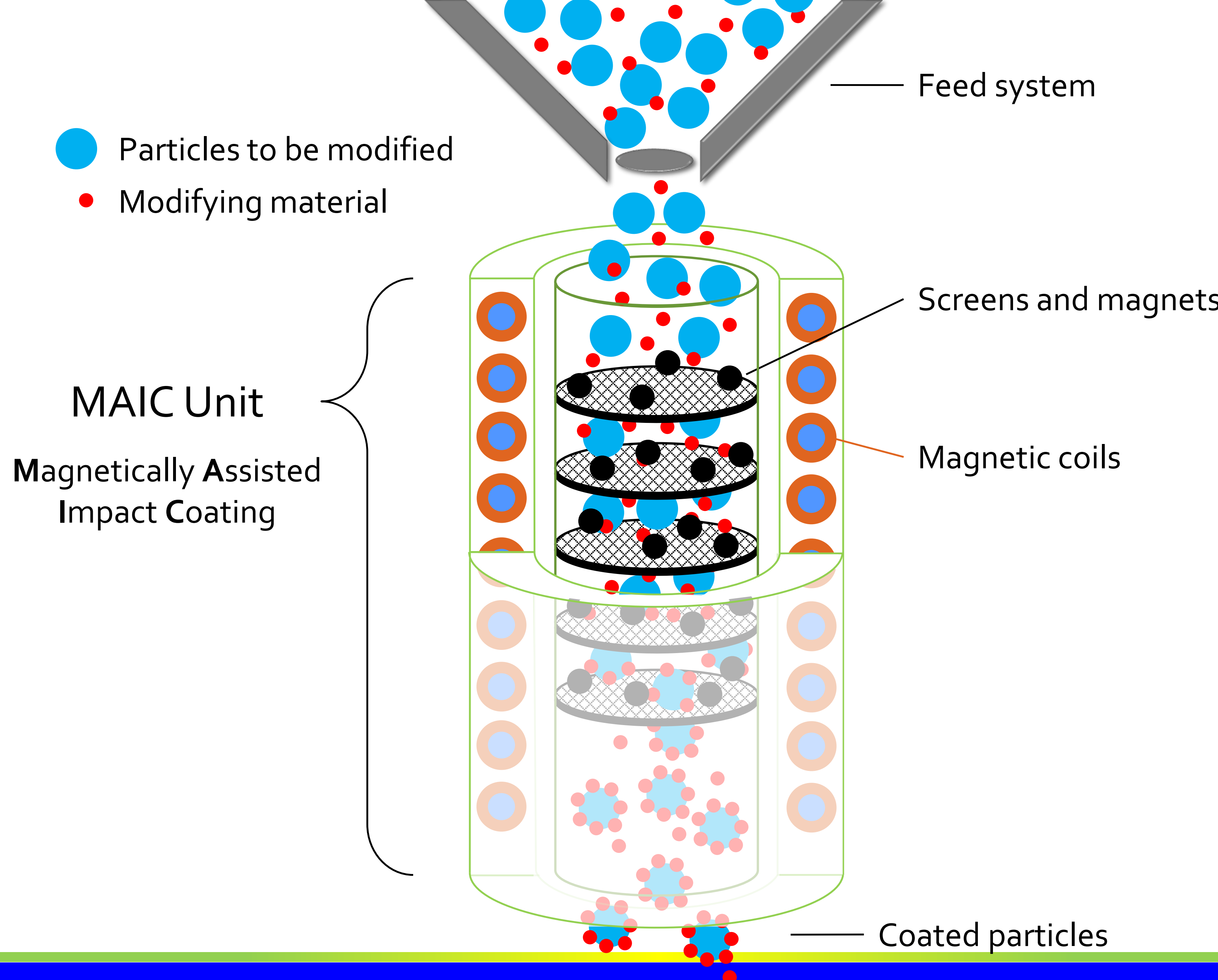


MAIC: Magnetically Assisted Impact Coating



Particle Surface Treatment:

- Add flow agents (silica)
- Coat with solids (TiO_2, ZnO)
- Distribute liquids (silanes)
  - US Patent 5,962,082
- Can be used for many applications and industries
  - Agriculture materials, cosmetics, pigments, catalysts


Feed system
Particles to be modified
Modifying material
Screens and magnets
MAIC Unit
Magnetically Assisted
Impact Coating
Magnetic coils
Coated particles

Experimental Parameters

Materials:

- *Citric acid monohydrate jet milled to 5 µm or Corn Starch*
- *Aerosil 200 Pharma, untreated fumed silica with 12 nm primary particle size*

Samples:

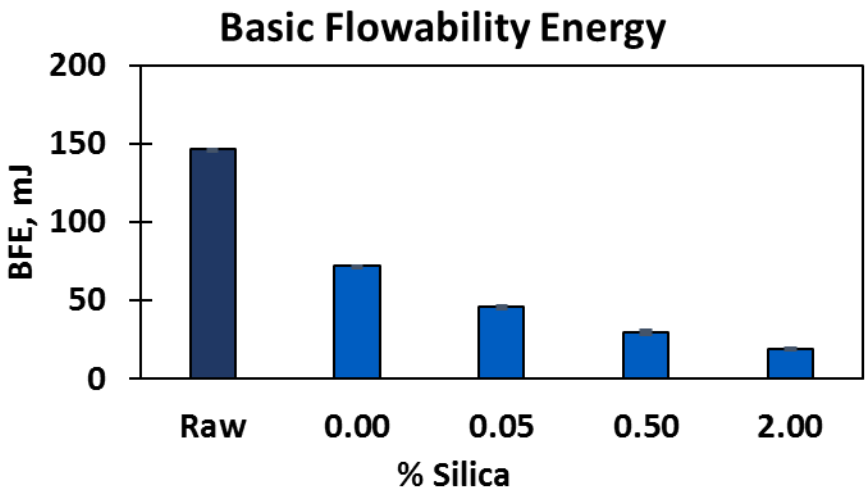
	B	C	D	E	A	G	F
% silica	0.00	0.00	0.05	0.50	2.00	0.50	2.00
Processing	None	MAIC	MAIC	MAIC	MAIC	V-blended	V-blended

Sample Preparations:

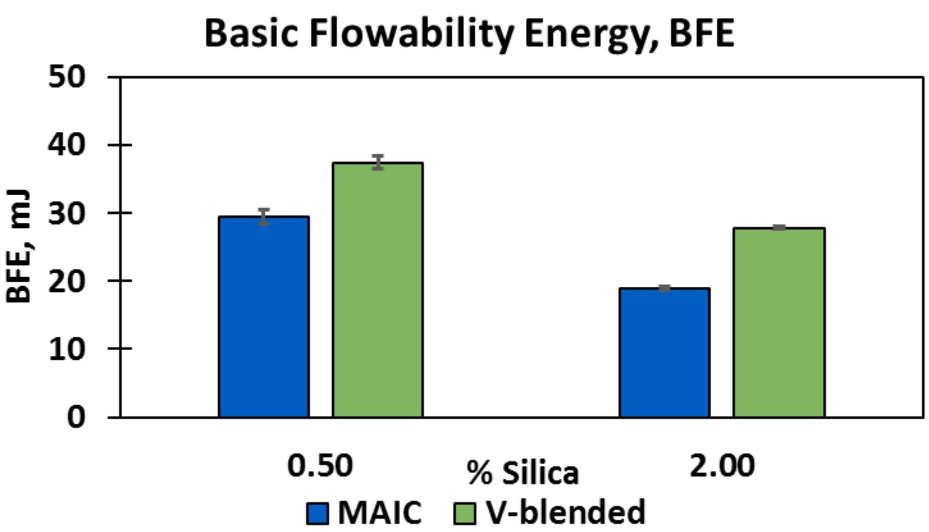
Citric acid or corn starch blended with 0-2 wt. % fumed silica in V-blender

Passed through MAIC or Set Aside

Flow Measurement Results for Citric Acid

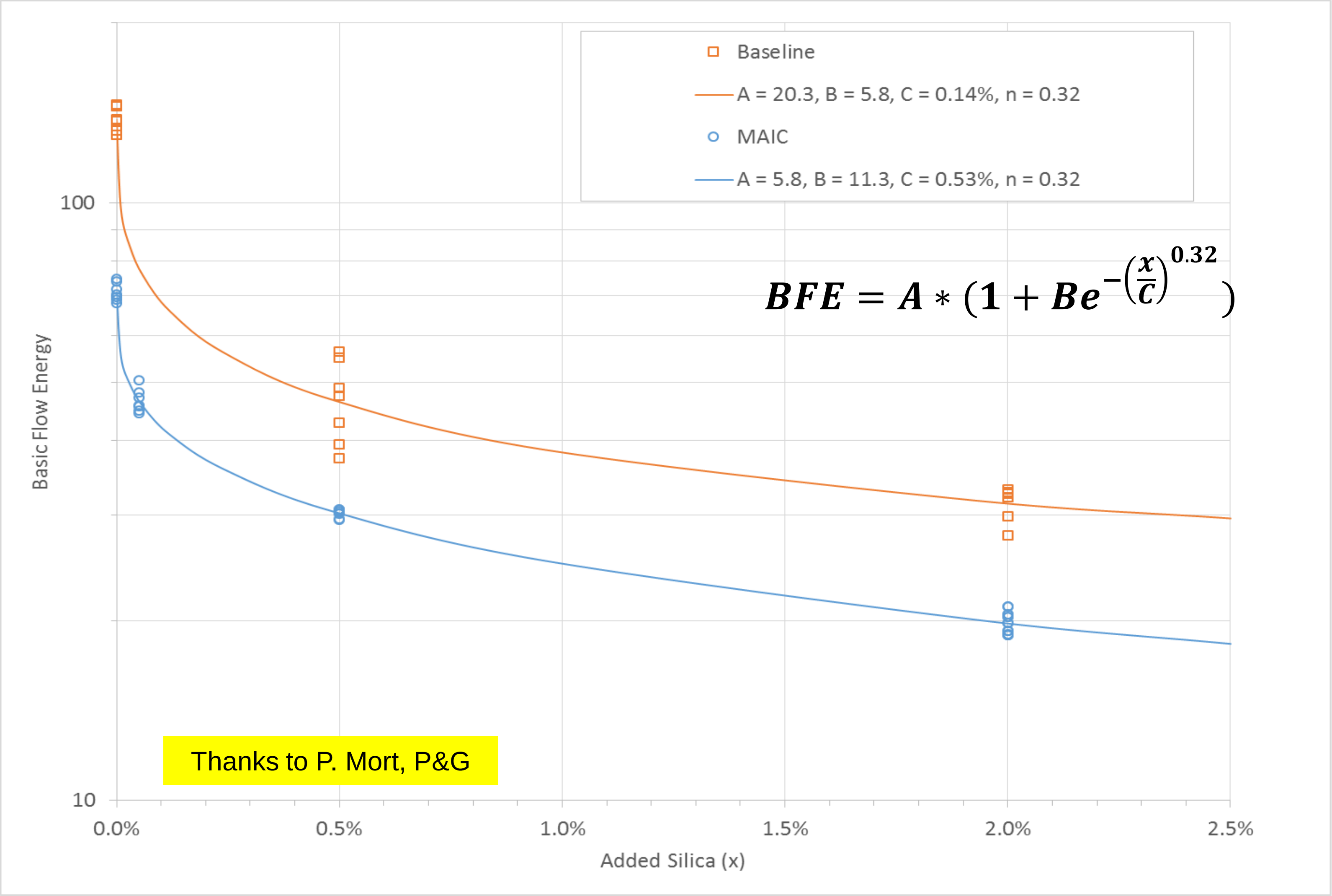


- Clear decreases in BFE with increasing % silica
- Marked decrease between the raw and MAIC treated sample (0% (w/w) silica)



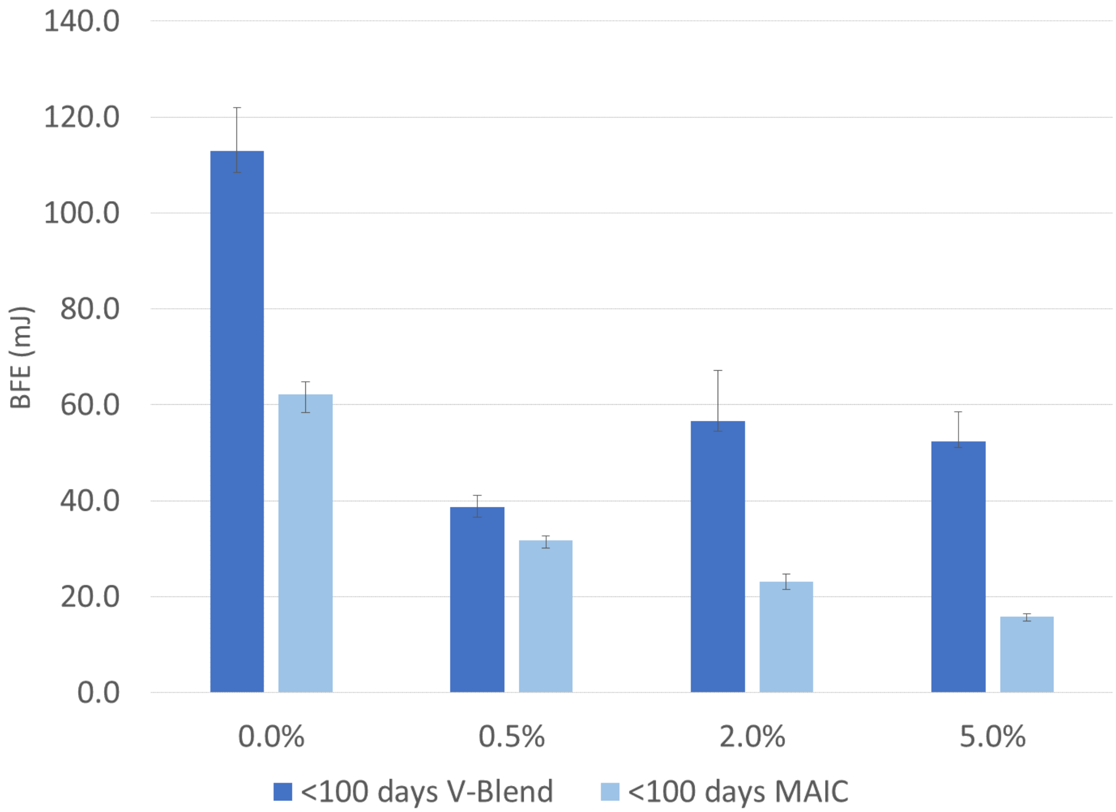
- At equal silica loadings, MAIC samples show lower BFE
- 0.5% MAIC and 2.0% V-blend near equal

Comparing MAIC to V-Blending



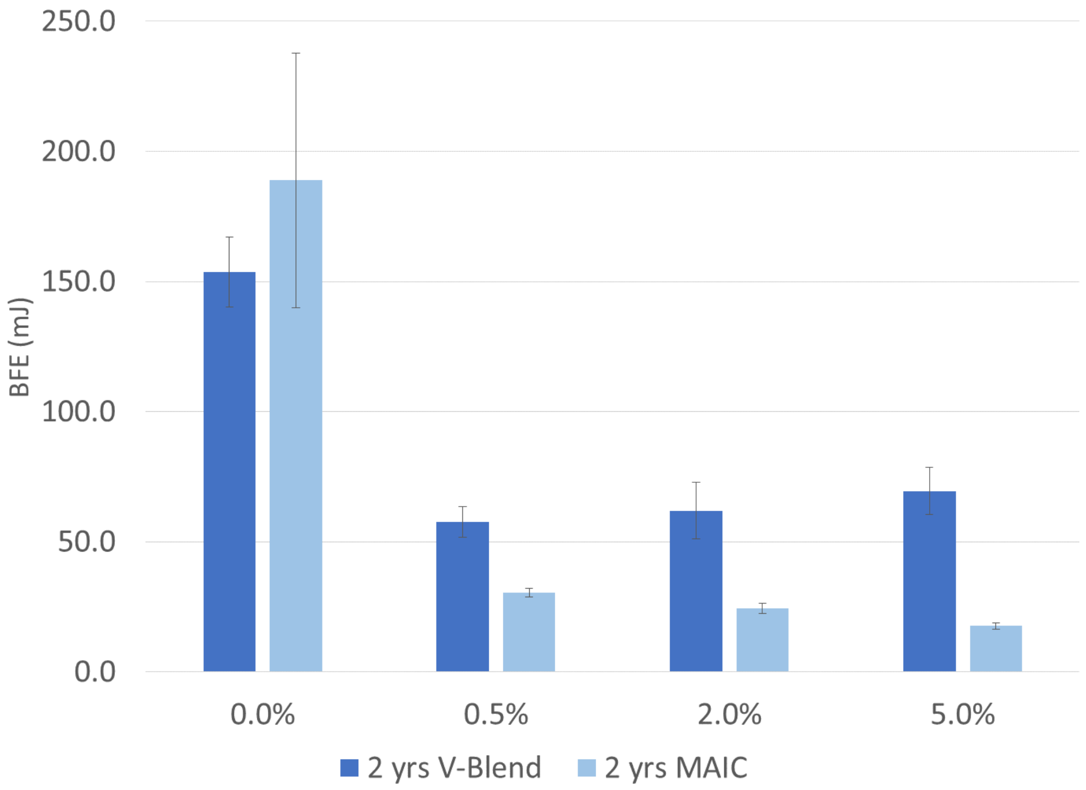
Citric Acid – Short Term

- MAIC processing initially yields a lower BFE in all cases
- Silica addition via v-blending does not improve BFE
- The mean difference between v-blending and MAIC for each silica loading level is significant at $p < .0001$.

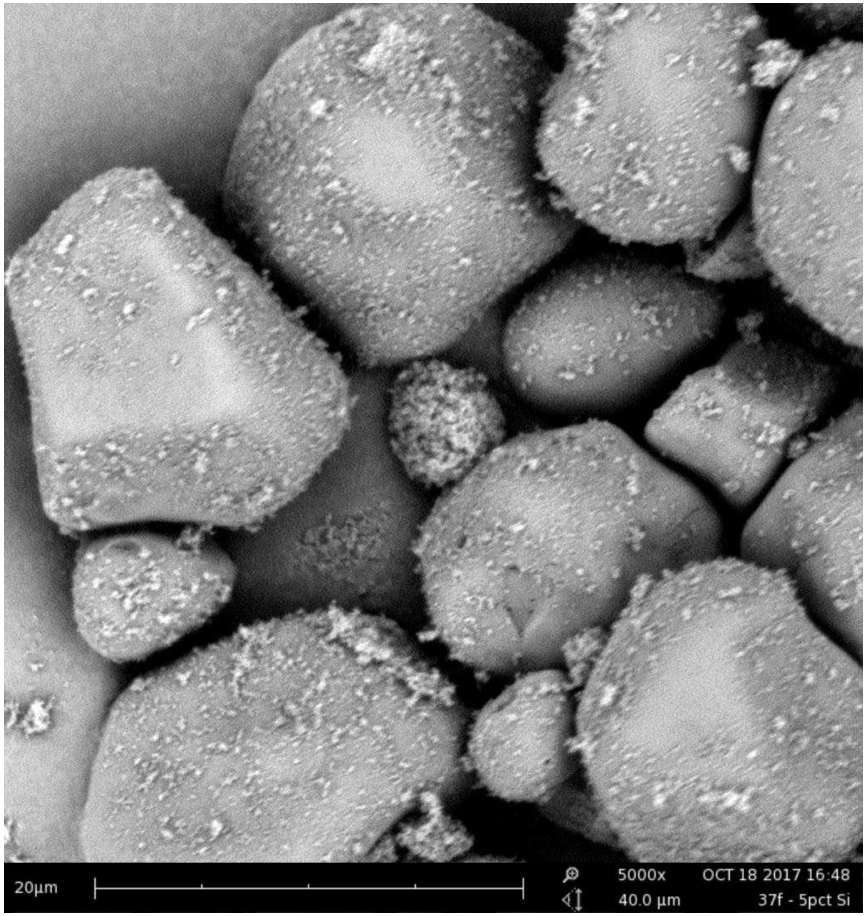


Citric Acid – Long Term

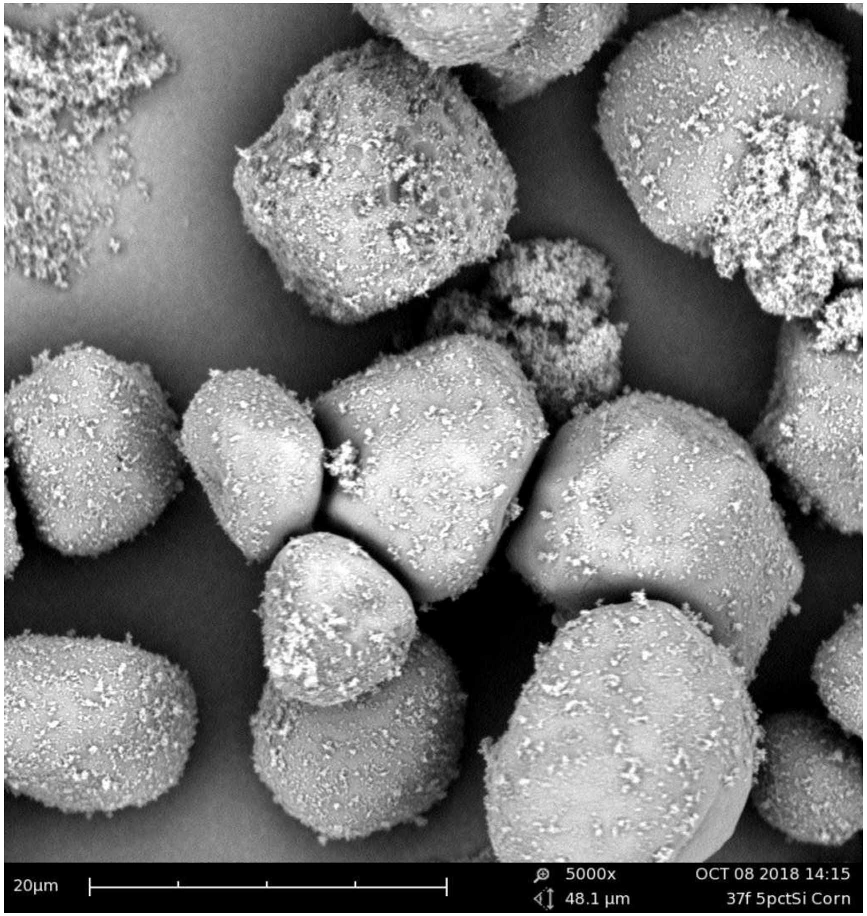
- MAIC-applied silica on citric acid maintains lower BFE than corresponding v-blend
- Addition of more silica does show improvement for MAIC samples ($p < .0001$, $r^2 = .64$)
- Divergent behavior observed for MAIC-processed citric acid without silica
- The mean difference between v-blending and MAIC for each silica loading level is significant at $p < .0001$, except for 0% silica ($p = .170$).



Cornstarch SEM Images



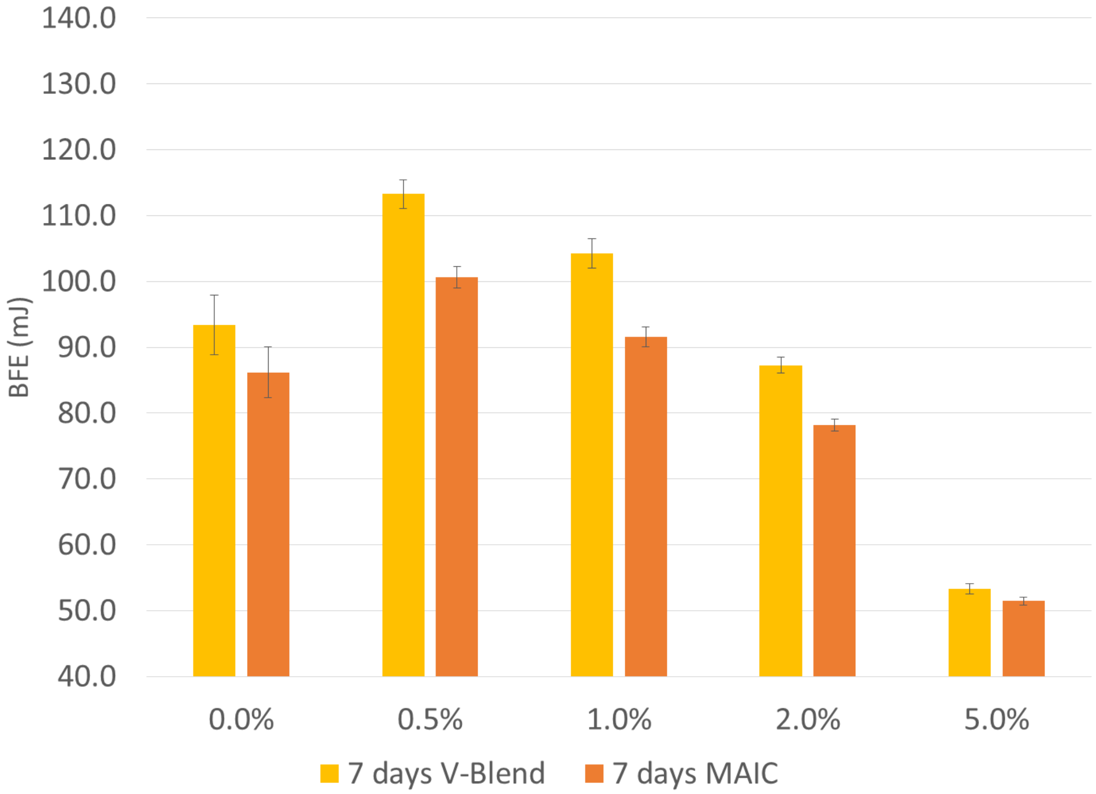
Cornstarch, 5% silica (MAIC), fresh



Cornstarch, 5% silica (MAIC), 1 year later

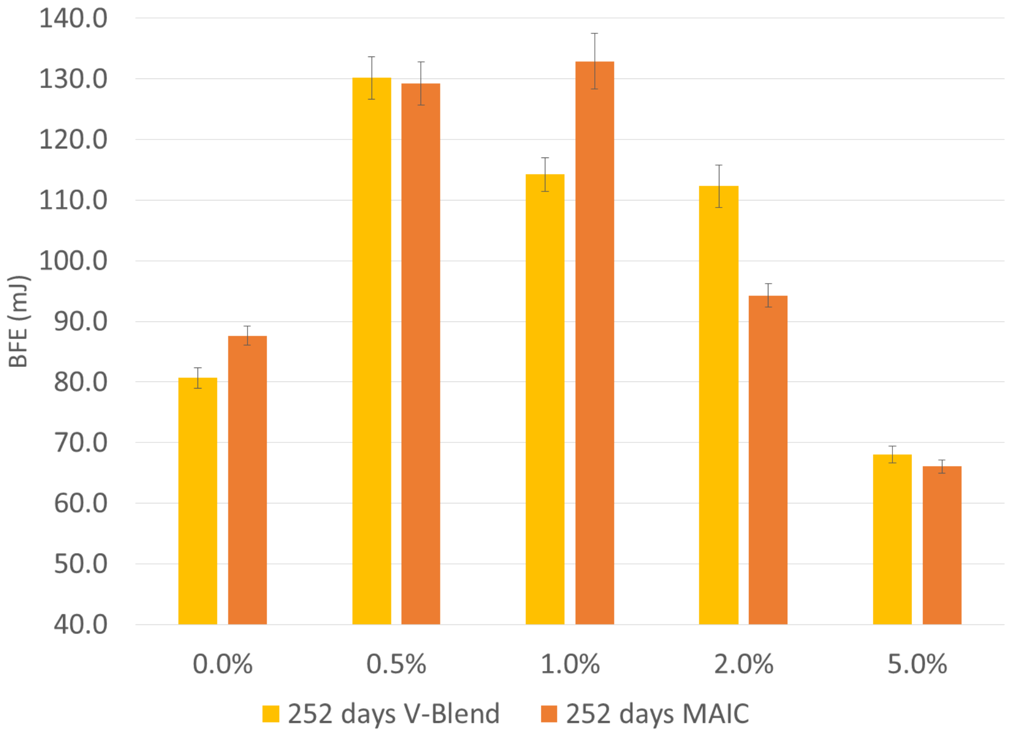
Cornstarch – Short Term

- Like citric acid, MAIC-processing initially yields a lower BFE in all cases
- The addition of small amounts of silica does not lower BFE
- The mean difference between v-blending and MAIC for each silica loading level is significant at $p < .05$



Cornstarch – Long Term

- After 9 months, the differences between MAIC and v-blending cannot be observed
- Processing effects appear to have worn off,
- Addition of silica does not appear to lower BFE except for the highest loading levels (5%)



Spray Drying of Materials with Waters of Hydration

Interested in Hydrated Inorganic and Polymer Precursors for Novel Material Production

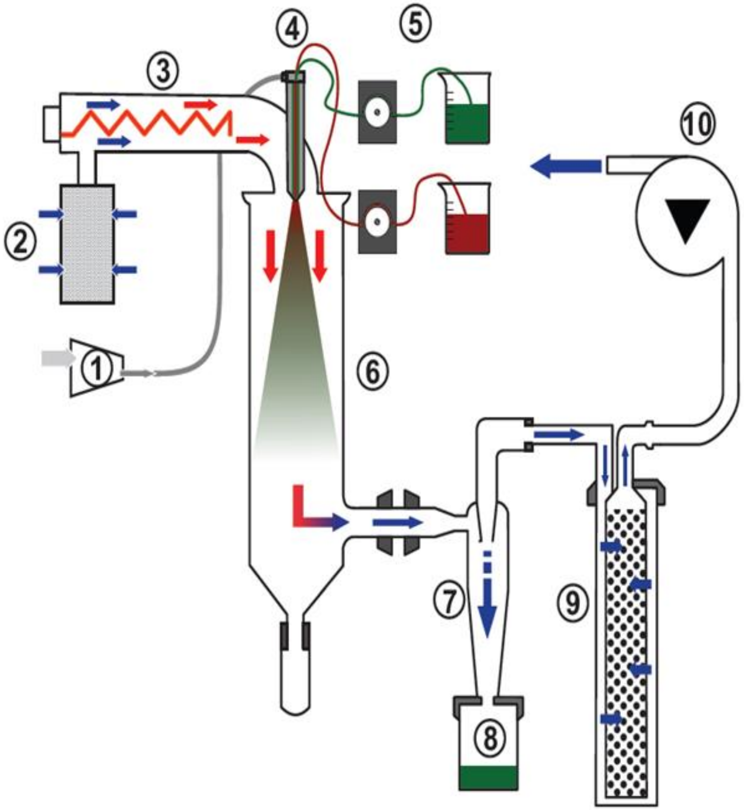
$Al_2(SO_4)_3 \bullet 18H_2O$

- For alumina based ceramics

$Na_2Succinate \bullet 6H_2O$

- For polyester type polymers

Typical drying conditions of 95 °C



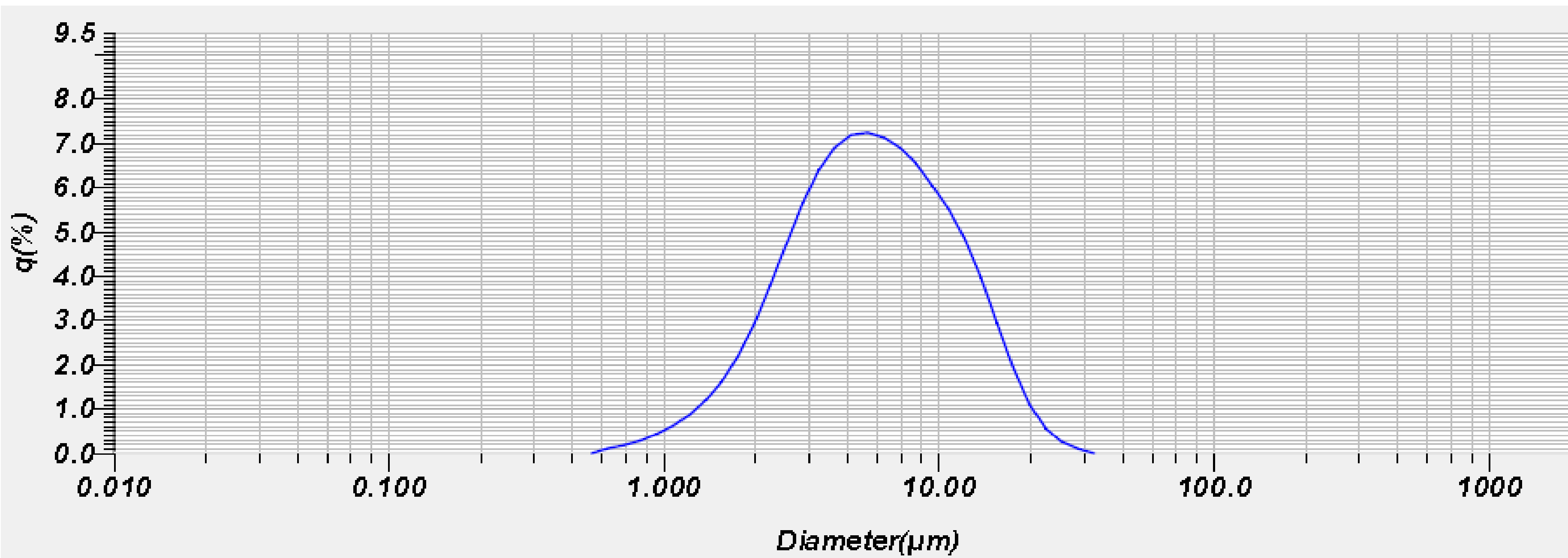
Particle Size Distribution (PSD):

Spray Dried Aluminum Sulfate NX326-13-01

Remarks 1 : IPA

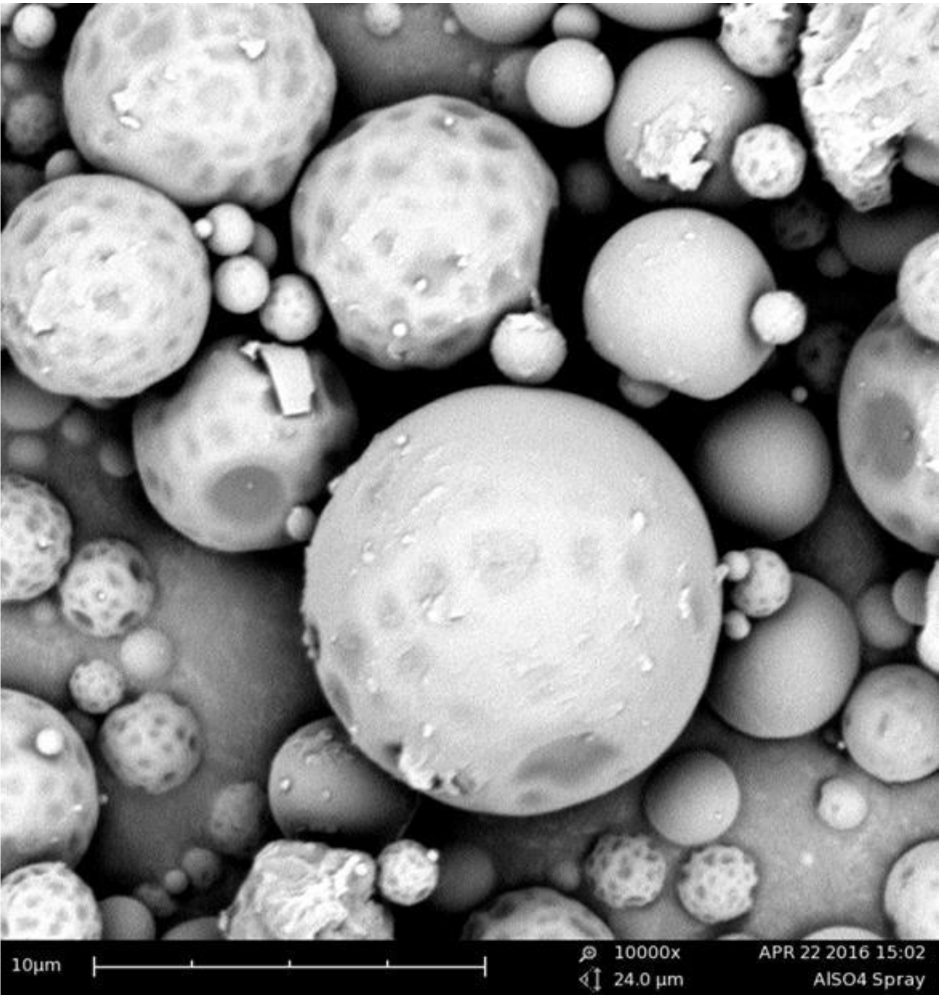
Mean Size	:	**6.94950(μm)**
Median Size	:	**5.62878(μm)**
Std.Dev.	:	**4.7652(μm)**
Mode Size	:	**5.4795(μm)**
S.P.Area io	:	**13926(cm^2/cm^3)**
Diameter on Cumulative %	:	**(1)5.000 (%)- 1.6910(μm)**
	:	**(2)10.00 (%)- 2.2327(μm)**
	:	**(3)50.00 (%)- 5.6288(μm)**
	:	**(4)90.00 (%)- 13.6195(μm)**
	:	**(5)98.00 (%)- 19.9238(μm)**

Cumulative % on Diameter	:	(1)10.00 (μm)- 78.407(%)
	:	(2)25.00 (μm)- 99.466(%)
	:	(3)50.00 (μm)- 100.000(%)
	:	(4)75.00 (μm)- 100.000(%)
	:	(5)100.0 (μm)- 100.000(%)
	:	(6)150.0 (μm)- 100.000(%)
	:	(7)180.0 (μm)- 100.000(%)

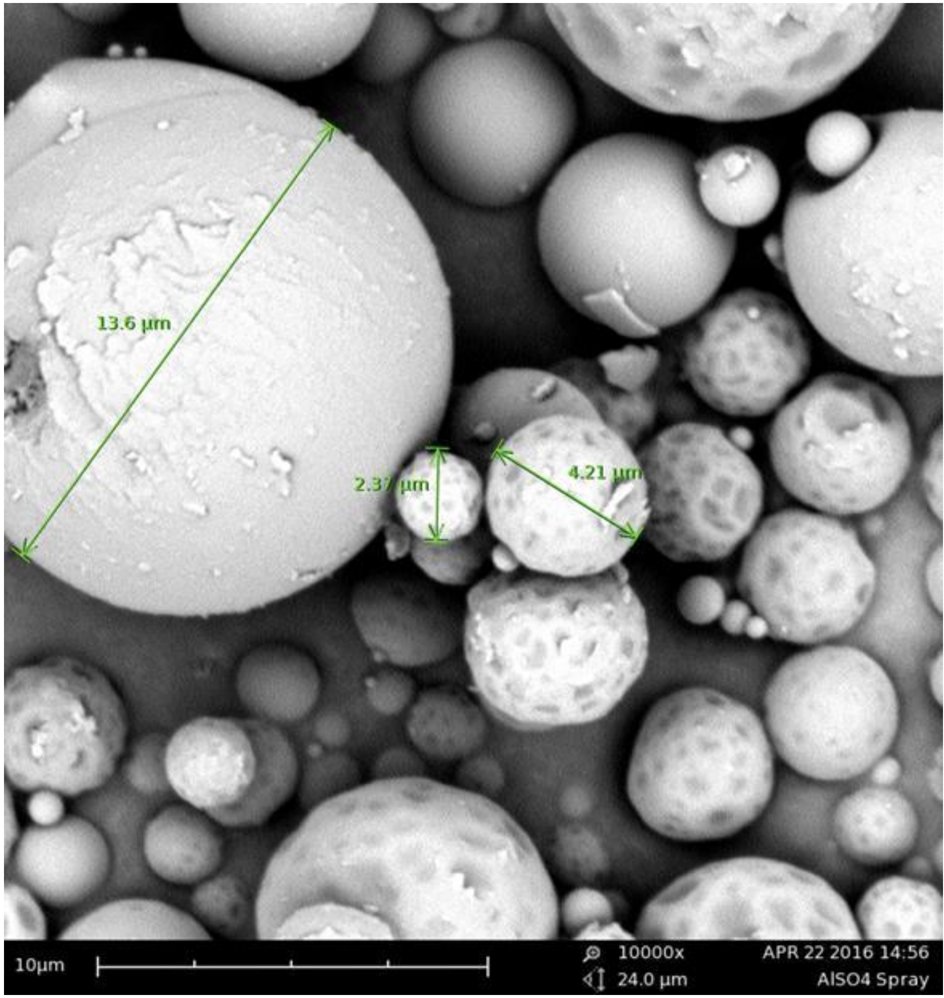


D_{10} = 2.23 μm **D_{50} = 5.63 μm** **D_{90} = 13.6 μm**

Spray Dried Anhydrous Aluminum Sulfate

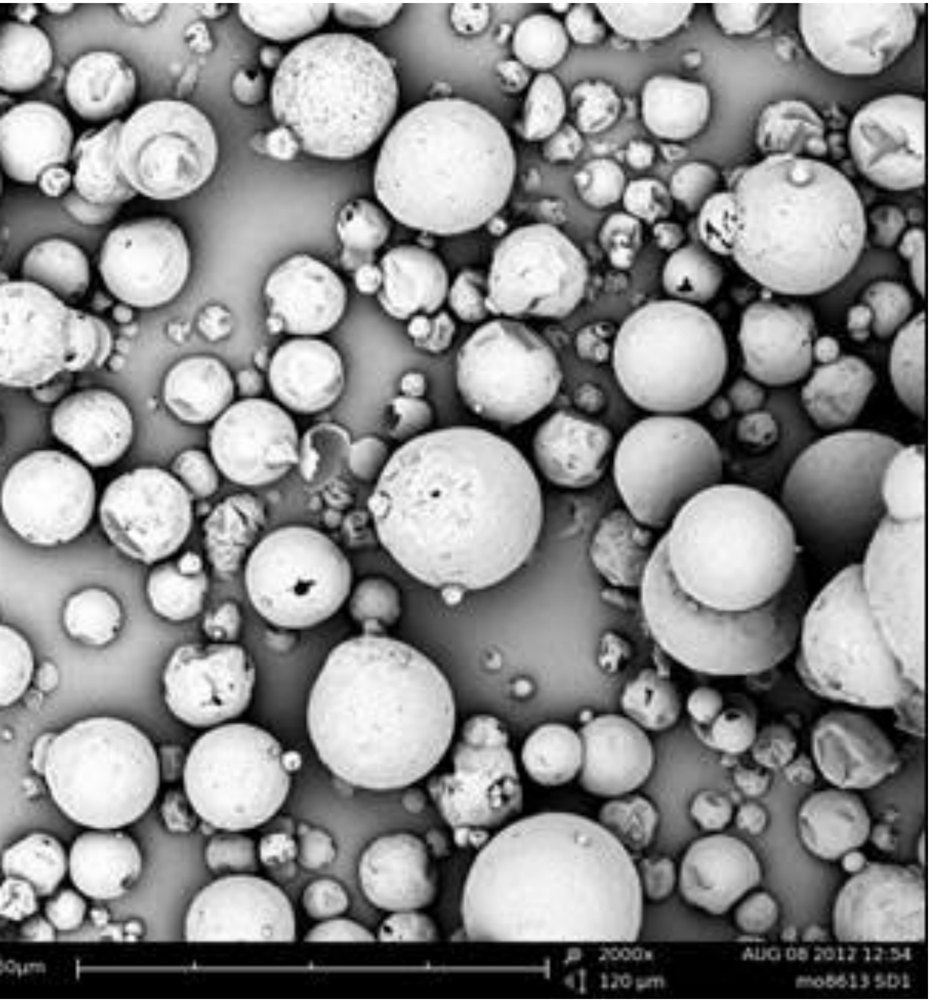


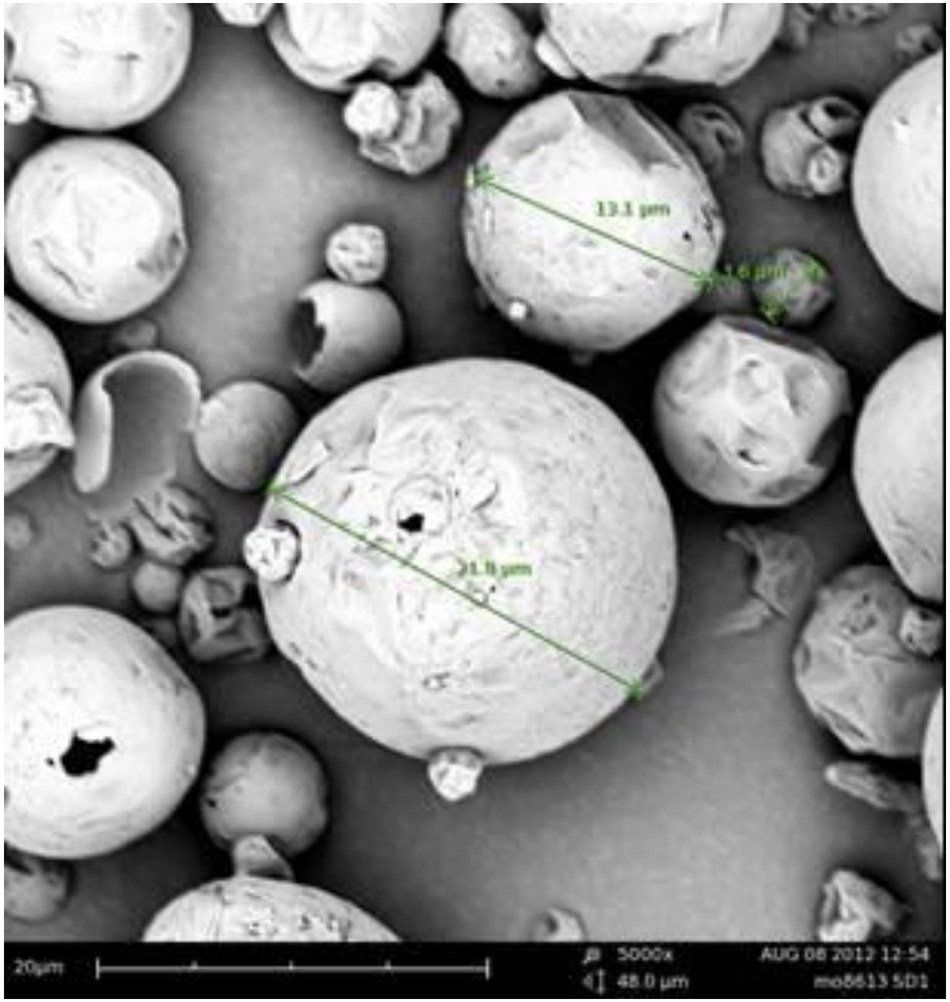
10,000 X



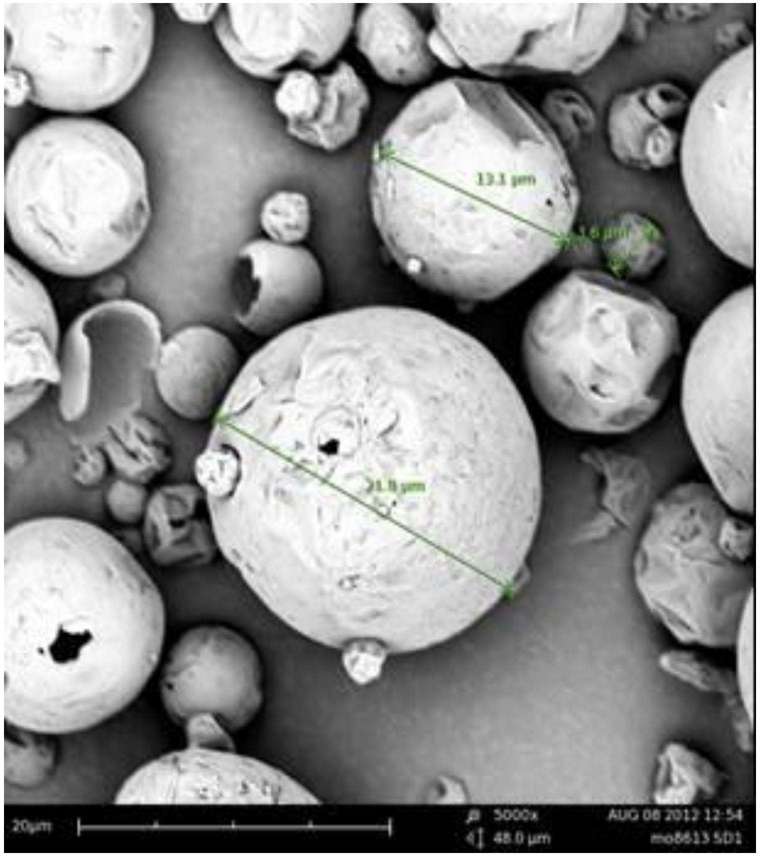
10,000 X

Spray Dried Anhydrous Na Succinate

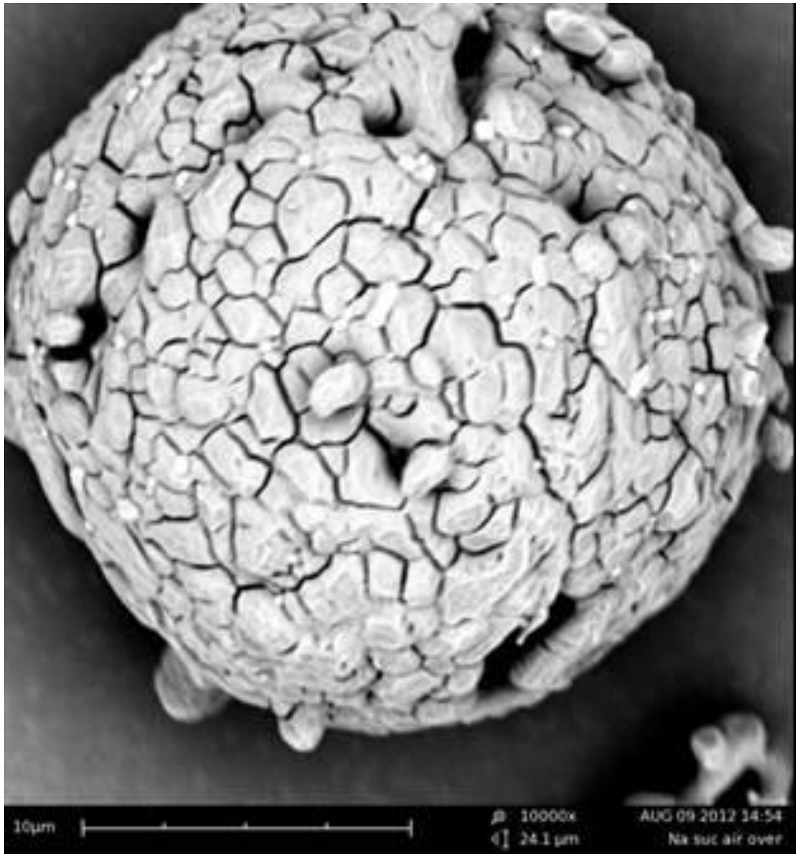




Ambient Aged Spray Dried Materials



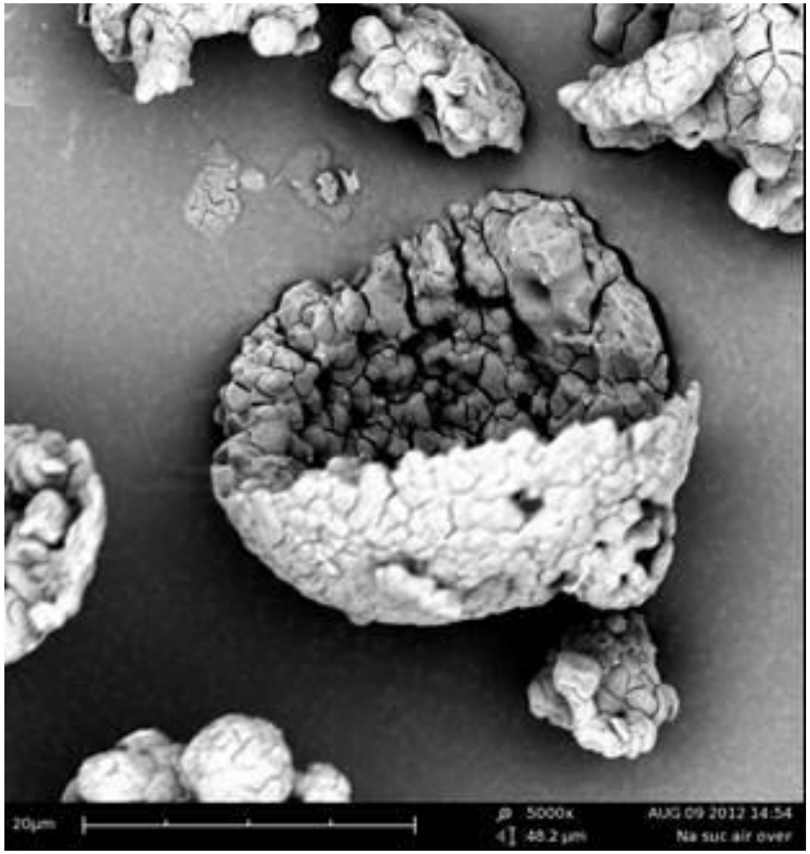
Anhydrous Sodium Succinate



Hydrated Sodium Succinate

Interior of Spray Dried Anhydrous and Hydrated Na Succinate

Anhydrous Na Succinate



Rehydrated Na Succinate

Corn Bran Overview

Corn Bran Composition

- Starch 1-10%
- Protein 1-8%
- Oils 0-2%
- Ash 1-6%
- Water 1-10%

Cellulose/Hemicellulose/Lignin Composition

- Cellulose 25-30%
- Hemicellulose 60-70%
- Lignin 1-6%

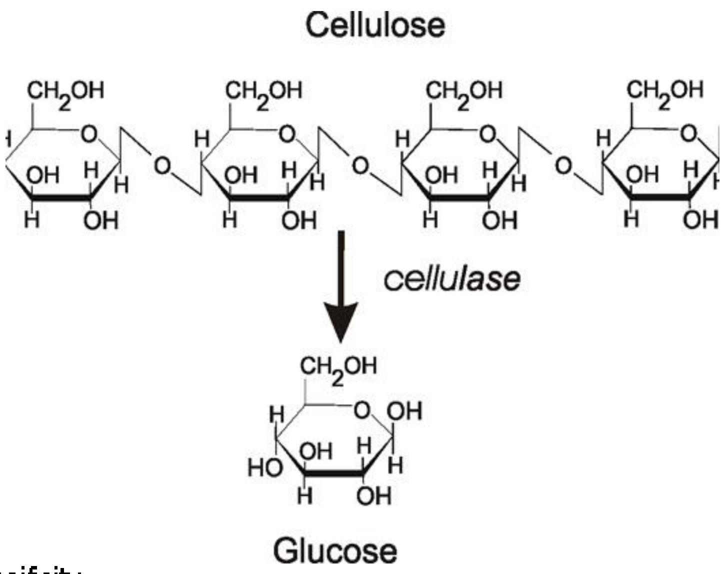
Material Characteristics

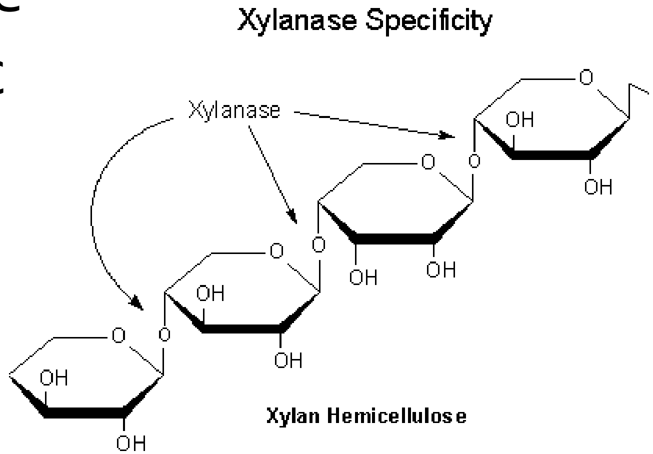
Cellulose

- Polymer of glucose
- Insoluble in common solvents
- Highly crystalline

Hemicellulose

- Polymer of Xylose
- Soluble in caustic





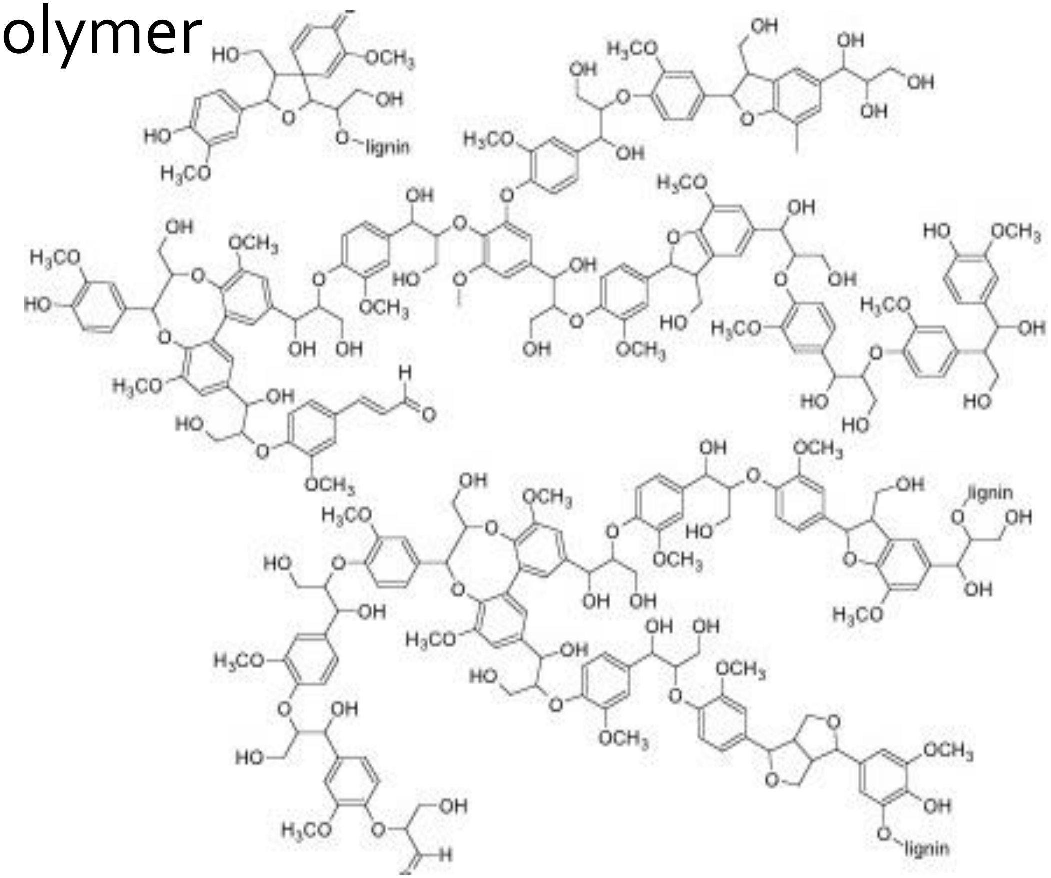
Xylan Hemicellulose

Polymer of β-(1-4)-D-xylopyranosyl units

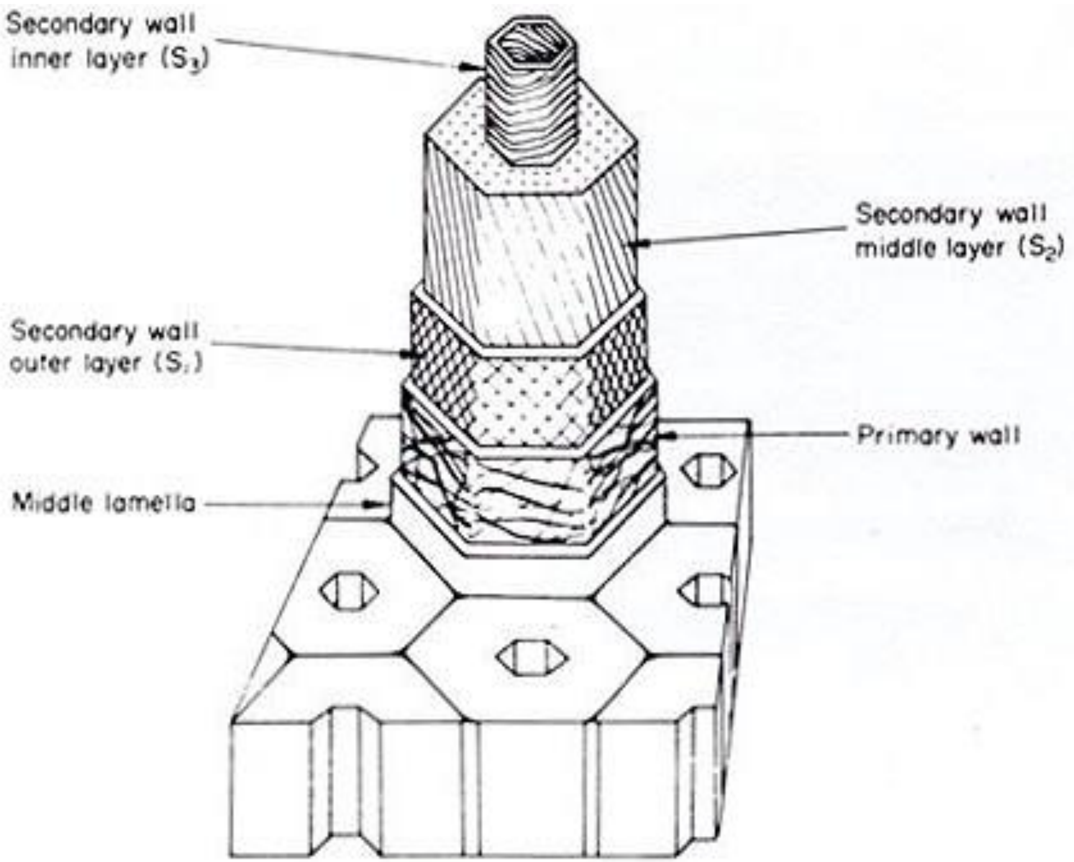
Material Characteristics

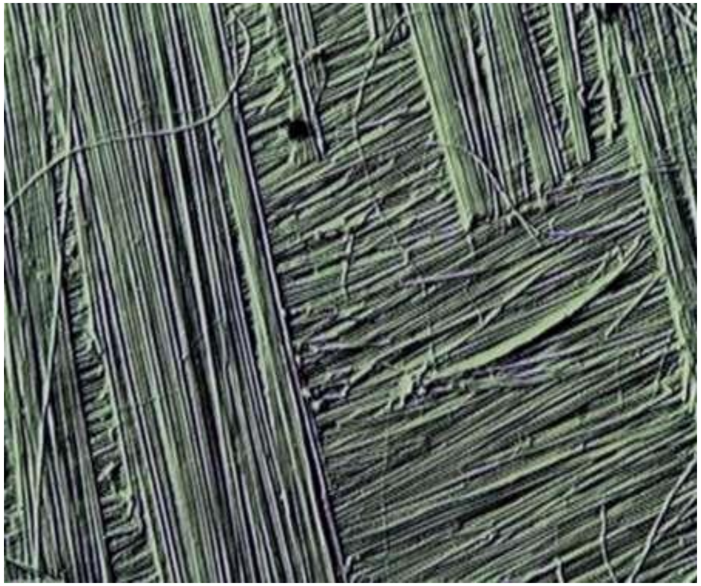
Lignin

- Cross-linked aromatic polymer
- Soluble in caustic
- Highly colored

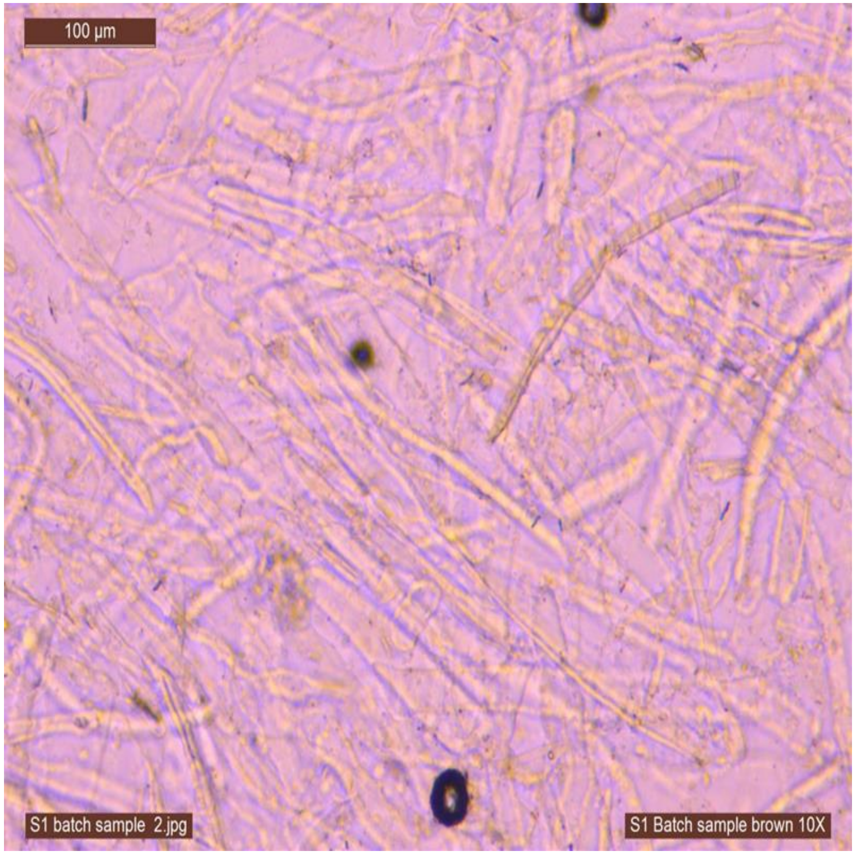


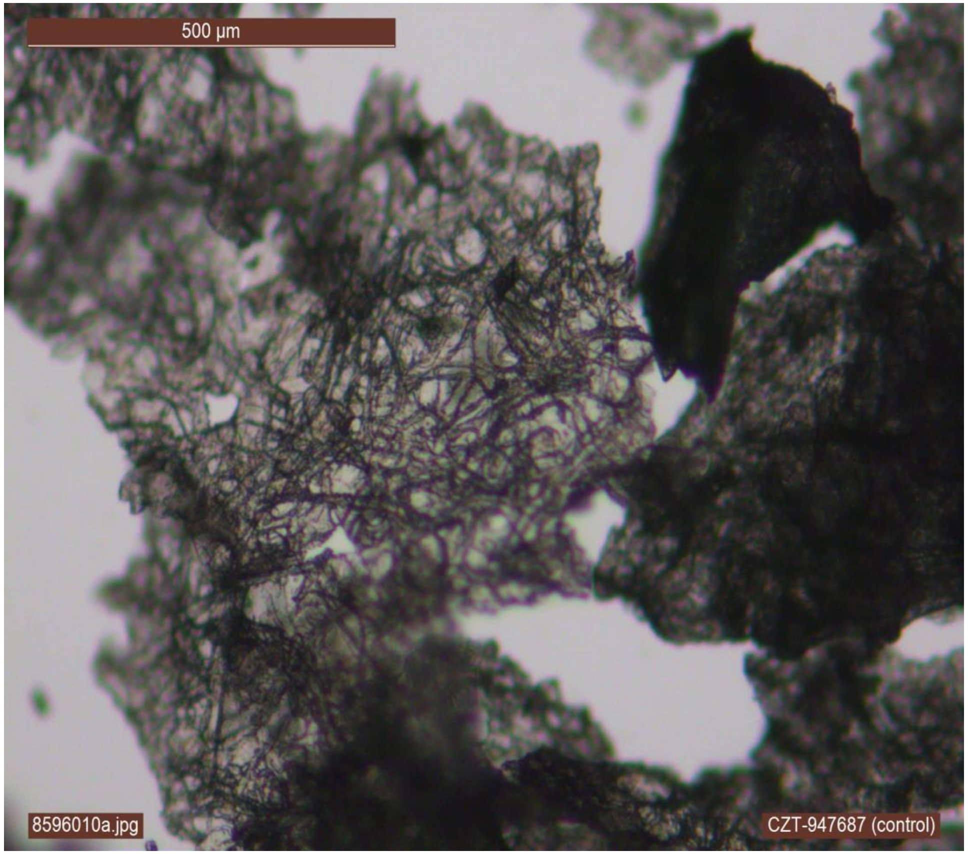
Fiber Structure





Cellulose Images





Compostional Analysis

TGA

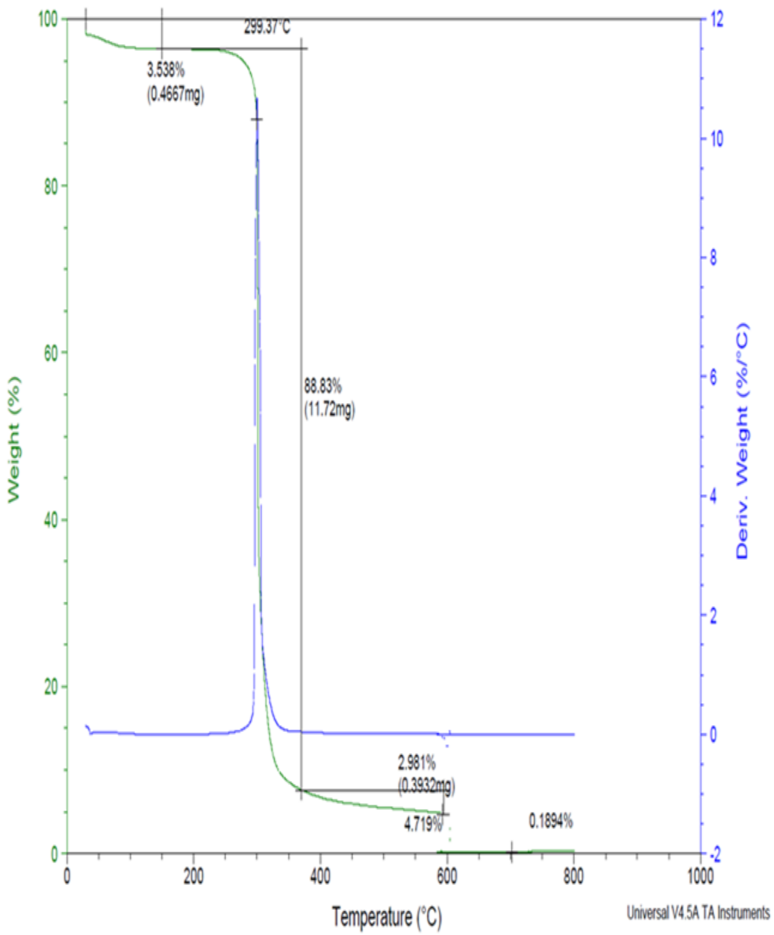
- Heat at constant rate
- Use high resolution option to measure weight changes
- Heat to 800 °C

Chemical Dissolution

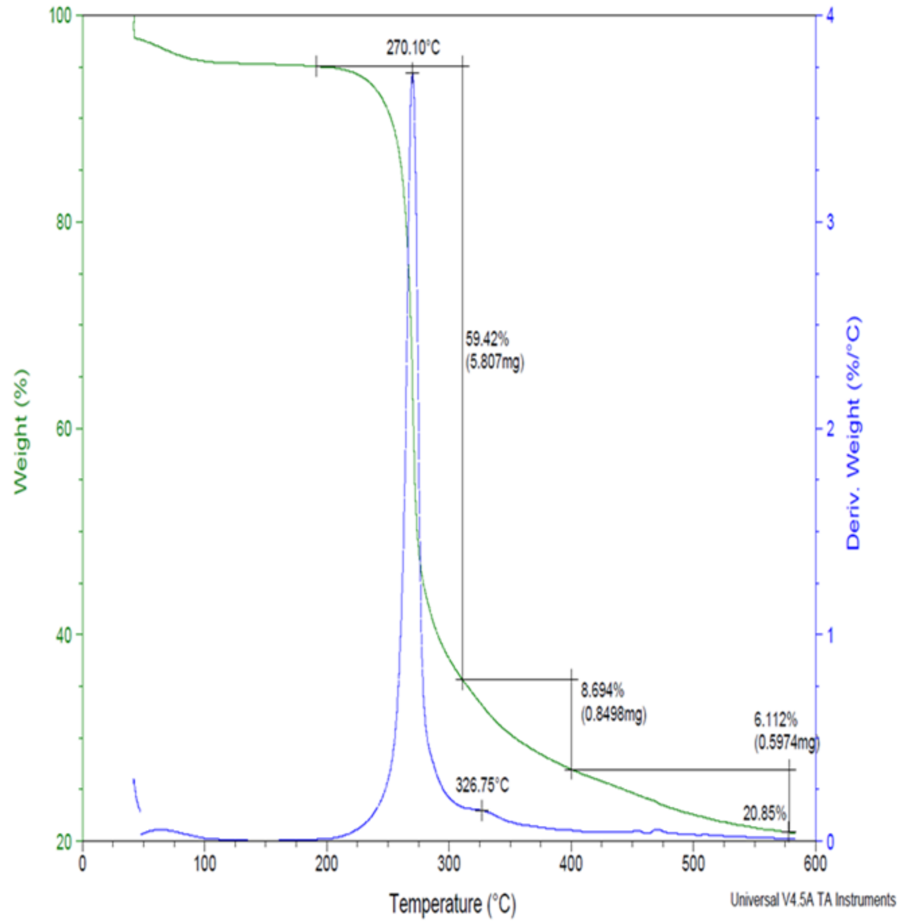
- Wash with detergent and water (water solubles)
- Wash with dilute sulfuric acid (hemicellulose)
- Wash with conc. sulfuric acid (cellulose)
- Ash at 500 °C (lignin)
- Remainder after ashing (ash)

TGA of Cellulose and Hemicellulose

Wood Cellulose

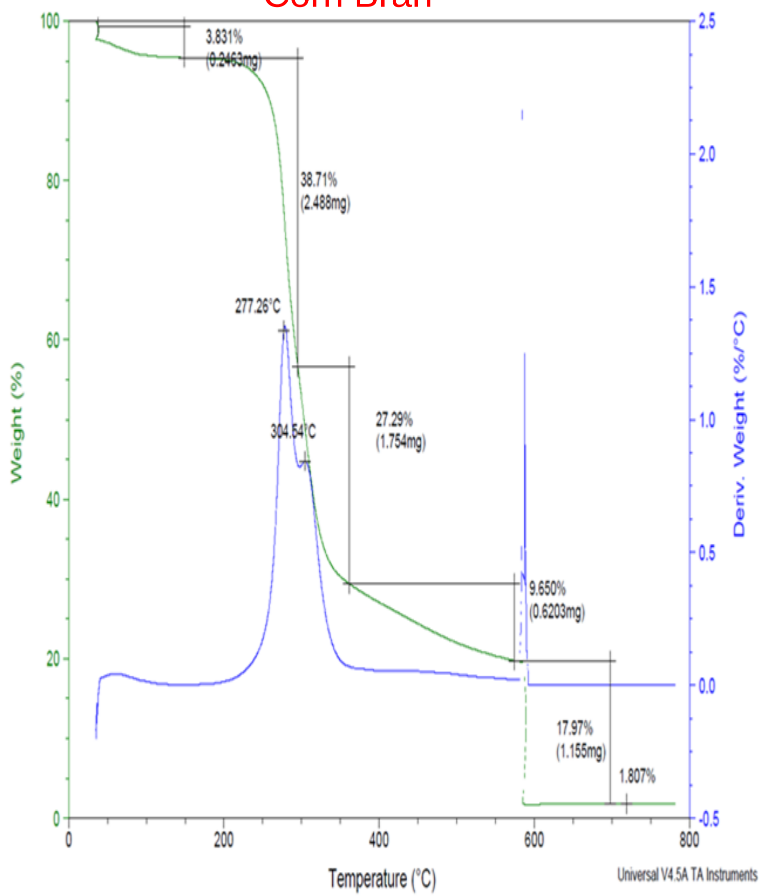


Hemicellulose

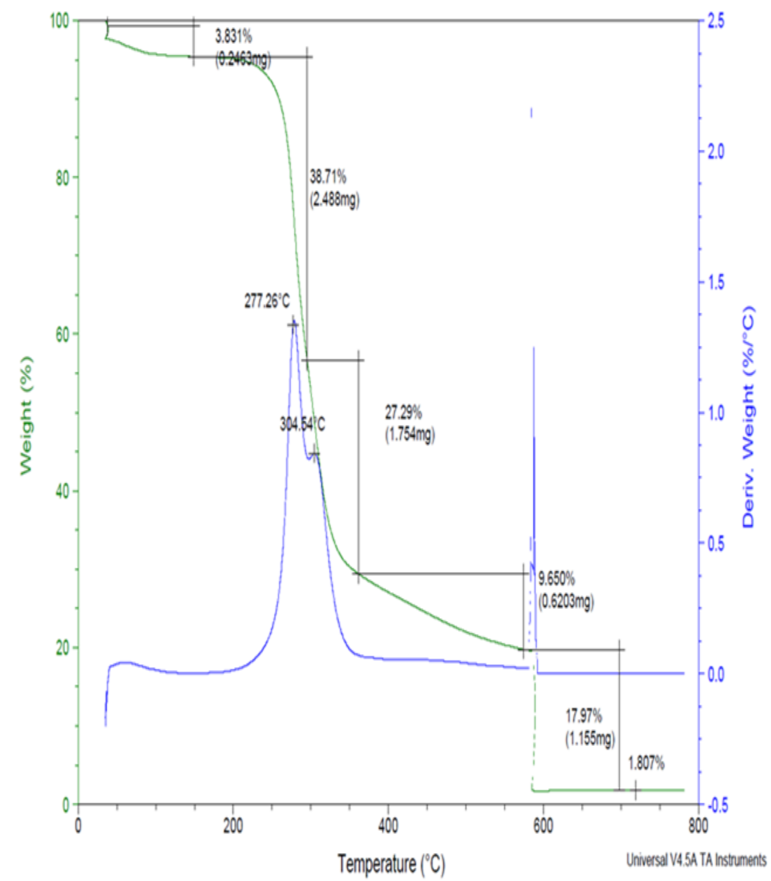


TGA of Corn Bran and Purified Cellulose

Corn Bran



Processed Cellulose

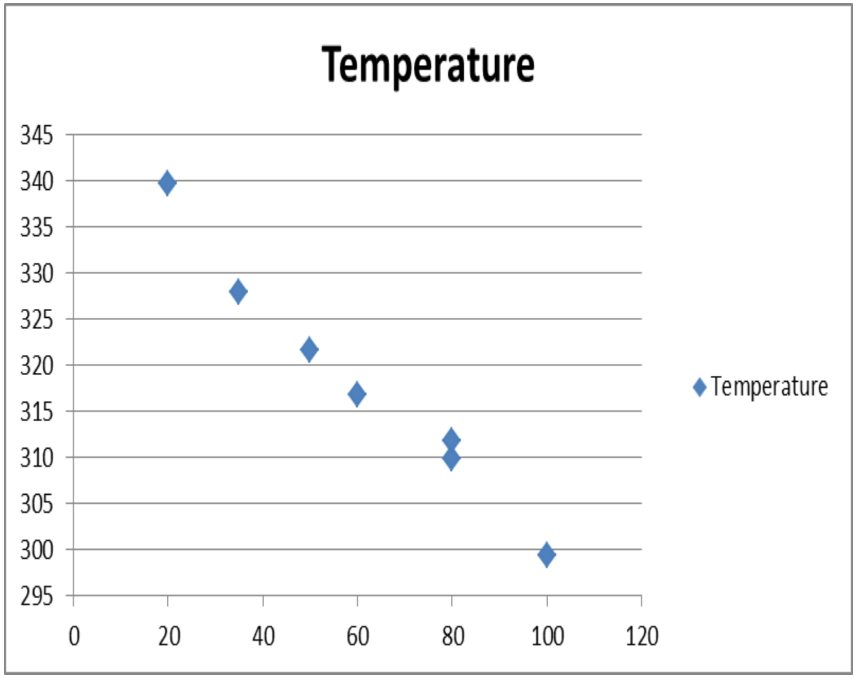


TGA Results

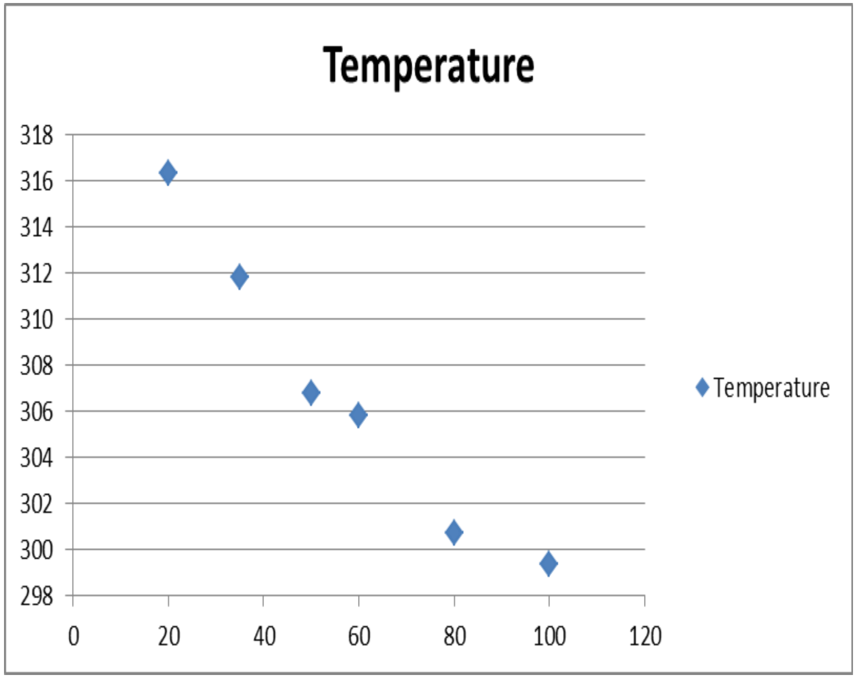
Sample	% Cellulose	Cellulose Decomp Temp
Cellulose	100	299.37
20/80 (H/C)	80	309.83
40/60 (H/C)	60	316.89
50/50 (H/C)	50	321.66
65/35 (H/C)	35	327.99
80/20 (H/C)	20	339.65
20/80 (S/C)	80	300.75
40/60 (S/C)	60	305.8
50/50 (S/C)	50	306.80
65/35 (S/C)	35	311.79
80/20 (S/C)	20	316.34

TGA Results

Hemicellulose Added to Cellulose



Starch Added to Cellulose



Impurity Characterization

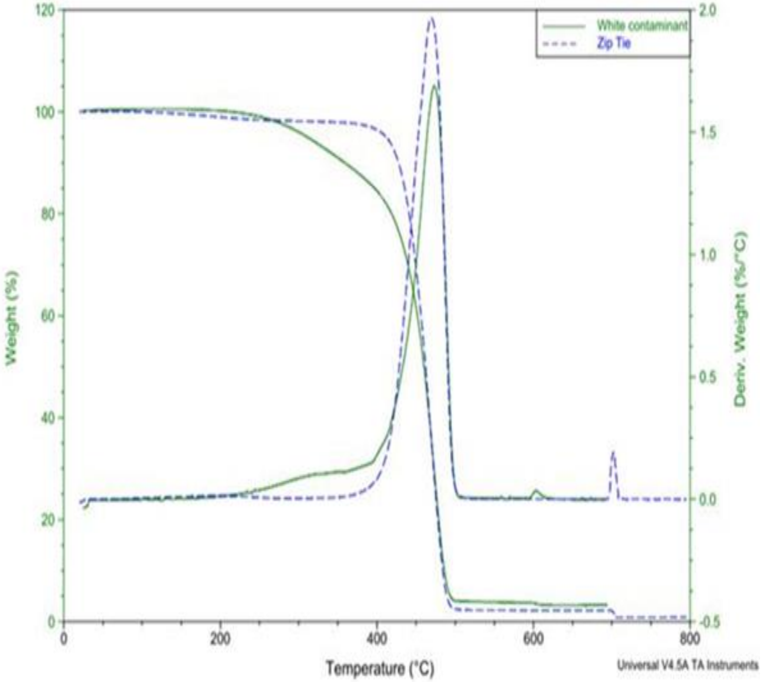
Optical Image of Impurity

Background Information

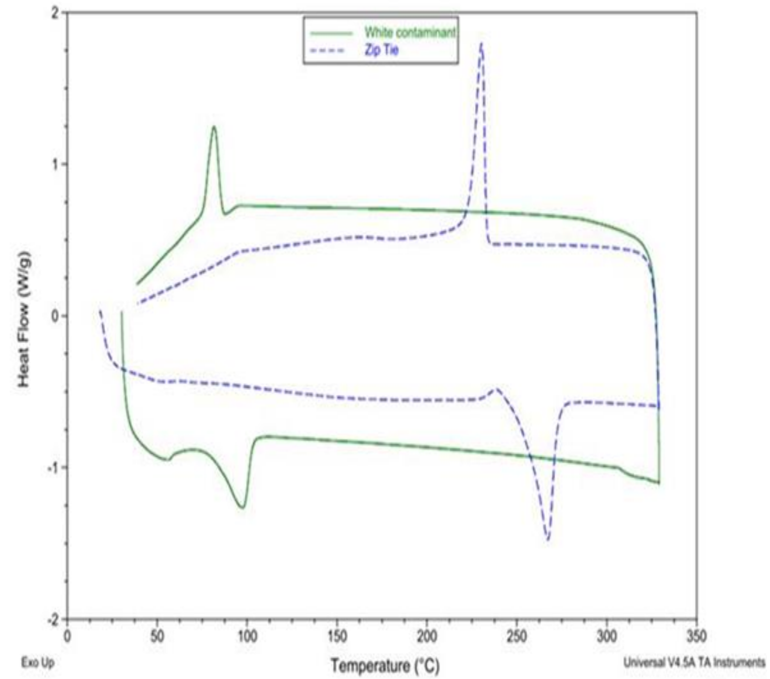
- Found by customer in product
- Potential for recall
- Process analysis done and potential contaminant Determined to be
  - Zip tie from equipment
  - Adhesive from customer's bag
- Characterization critical for understanding

Impurity Characterization

TGA Comparison

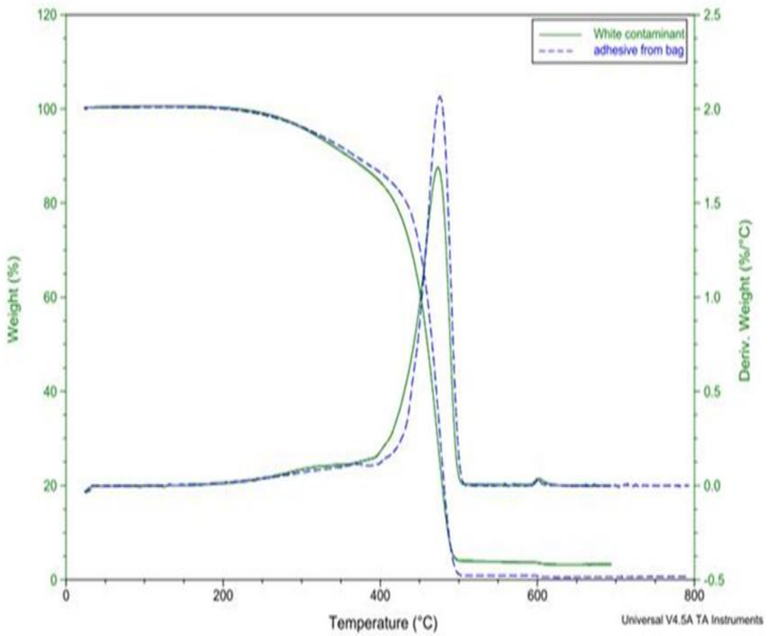


DSC Comparison

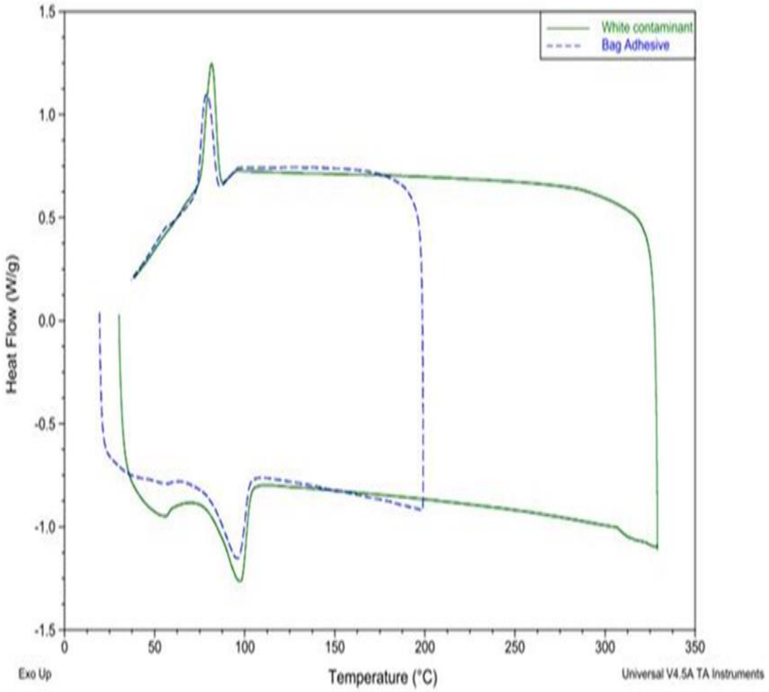


Impurity Characterization

TGA Comparison



DSC Comparison



Summary

- Characterization is critical to meet product and customer needs
- Multiple methods should be considered for most complete understanding
- It is hard to analyze too much

- Contact Information:
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  - whendrickson@aveka.com
  - 651-730-1729