Reactor Design for TiO_2 & SiO_2

a. Basics: How chemistry can affect particle size
b. Computational Fluid-Particle Dynamics (CPFD)
c. Scale-up of novel flame reactors

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Sponsored by the
Swiss/U.S. National Science Foundation & Degussa

Applications

Paints

Niche Fields:

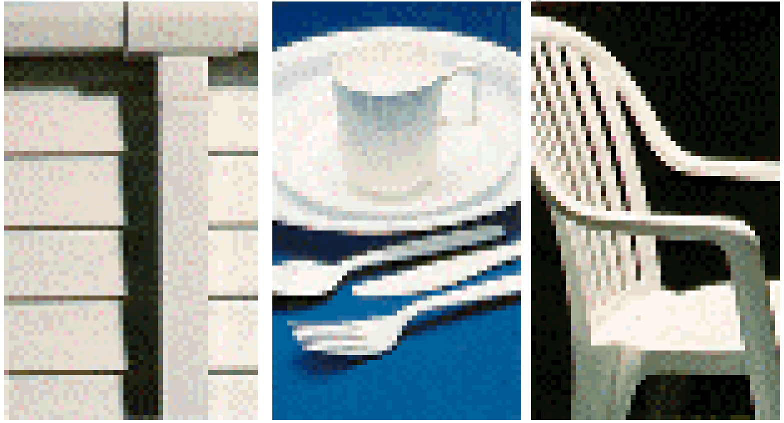
Catalysts, Sensors,

Photocatalysts,

Cosmetics etc.

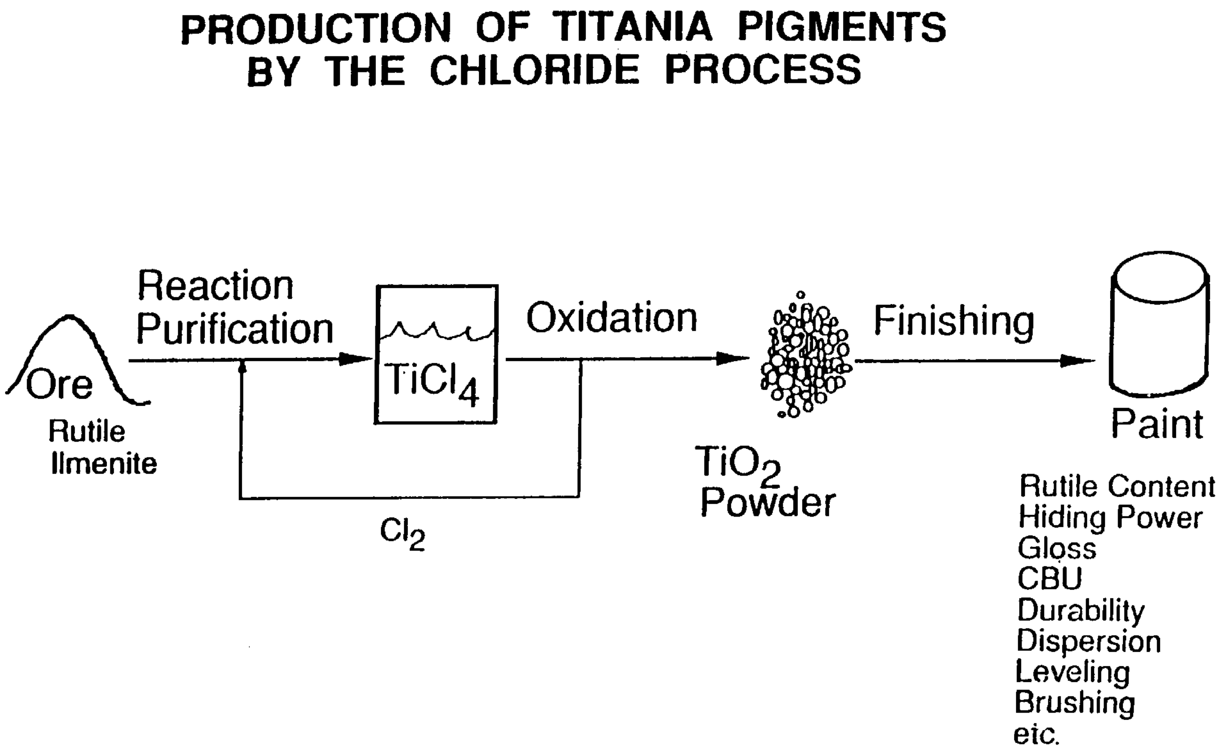
TiO_2 (titania)

Plastics coatings



Paper coatings

Production of Titania Powders



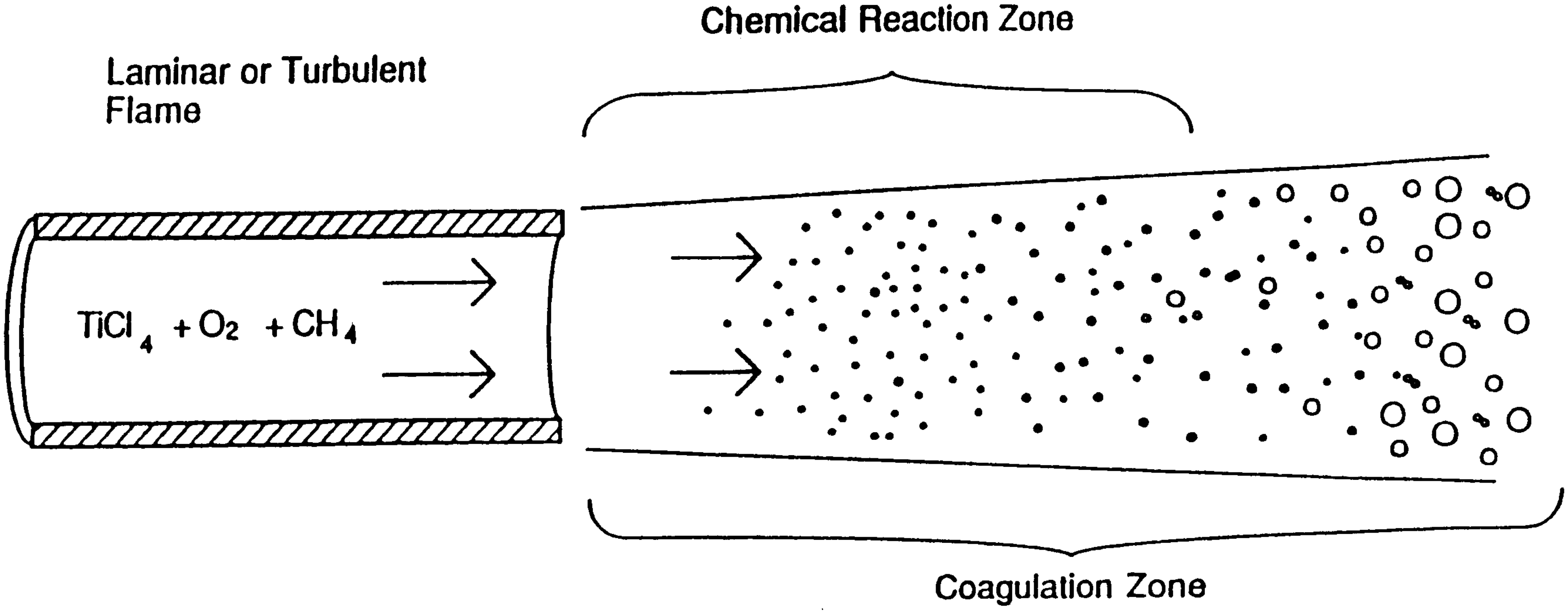
PRODUCTION OF TITANIA PIGMENTS BY THE CHLORIDE PROCESS

1 Facts

After characterization of the product of your competitor it is clear that he puts in the market a better product than yours. There are rumors that he may reduce his price also and this might threaten your market share. Furthermore, some of your colleagues in your chemistry research laboratory say that with “small” modifications you can make a series of new products.

2 Goal

To better understand the existing large flame reactor producing titania, silica or carbon black powder at high production rate (25 ton/h) so you can readily modify it or quickly build a new one to meet market demands.



3 Outlook

Examining historic records in the company proves to be a hard task on understanding how process variables affect the product. You see, every year small changes were made in the process by different people over the years. As a result, original designs and systematic experiments have little relevance with the current unit. In other words a huge reactor has been built through a series of trial and error procedures.

Today the reactor works very well but over a narrow region of conditions giving a narrow range of products.

The production engineers are reluctant to let you make any experiments on the production reactors. After all, the sales office has sold the production already for the next 9 months. They may think also that you are a “new” engineer fresh out of school who has no idea of the “real world”.

Experiments in the production reactor are “off limits” as any mistake can lead to large amounts of product outside specifications (imagine if it takes a couple of hours to realize that your particles are 15% bigger than that the required size you have 50 tons of titania or silica that you cannot sell or dispose. You are stack with it!).

4 Action

Basic studies need to focus on understanding the effect of process variables (precursor concentration, process temperature and residence time) on the product characteristics (primary and aggregate size distribution, crystallinity, morphology):

1. Temperature and residence time distribution in the production reactor.
2. Aggregate particle formation and growth

4.1 Chemistry

Literature review on reaction rates and particle formation. Assume that you are dealing with titania production by oxidation:

$TiCl_4$	+	O_2	TiO_2	+	$2\ Cl_2$
1 mol		1 mol	1 mol		2 mol
22.4 l		22.4 l	80 g		44.8 l

As the density of is 4 g/cm^3 the solids volume fraction is ϕ = (80/4)/44800 = 4.46x10^{-4}. This means that the particles may not affect the transport properties of the gas so the particle dynamics can be decoupled from the fluid dynamics and studied separately. Is this always true?

4.2 Selection of apparatus

Experiments can be done in a flame reactor. However this should be done with care as in flames the temperature changes rapidly and the residence time distribution does not easily scale as it is coupled to the temperature distribution.

For basic studies esp. when reaction rates are sought, a hot-wall reactor can be used also where the process variables can be easily separated. In addition the correspondence between flame and hot-wall reactors has been established in the literature.

Basic models for particle dynamics with population balance equations should be tested with data from either reactors. These models then can be interfaced with fluid and temperature and velocity profiles of the laboratory or production reactor and build a process simulator.

4.3 Simulator for Particle Formation and Growth

A simulator accounting for the detailed particle dynamics in the production reactor must be developed to achieve:

a) Better process control for existing products

(which process variables most effectively determine product powder characteristics and lead to better process yields that would translate into money and energy savings).

b) Acceleration of scale up for manufacture of new products

(a much better starting point for selection of process conditions rather than relying on empiricism and trial and error).

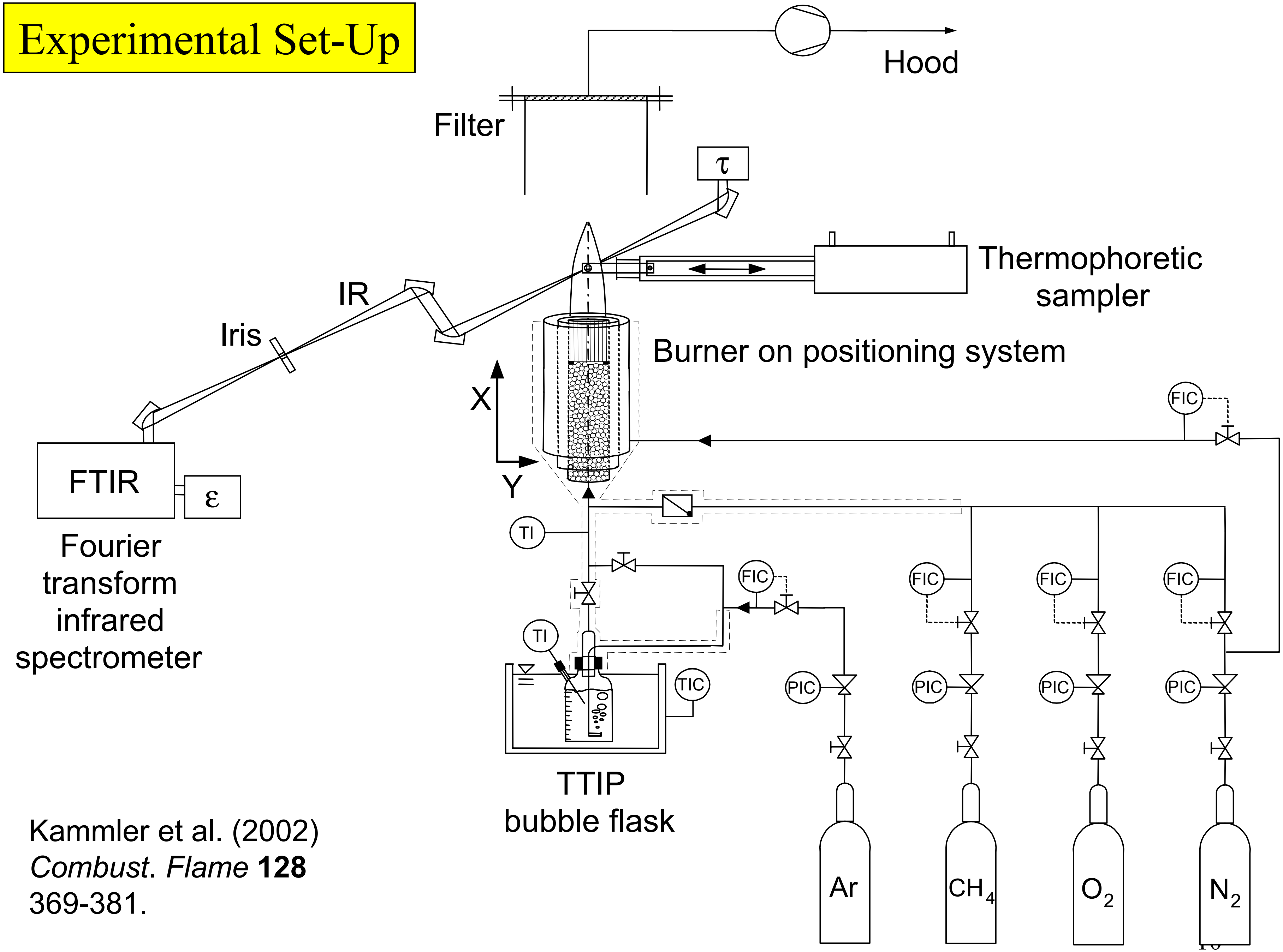
c) Reduction of the down time of existing production lines

(process conditions prone to particle deposition on reactor walls can be identified).

d) Education tool for personnel

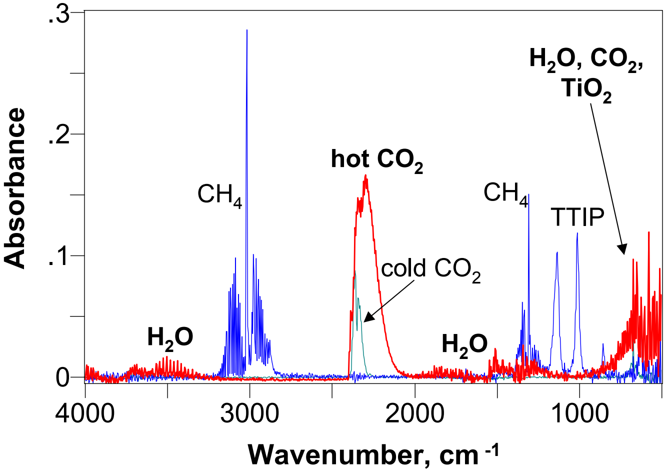
(training of new scientists and engineers for research and development as well as reactor operators at reaction sites contributing to safety and environmental compliance).

Experimental Set-Up



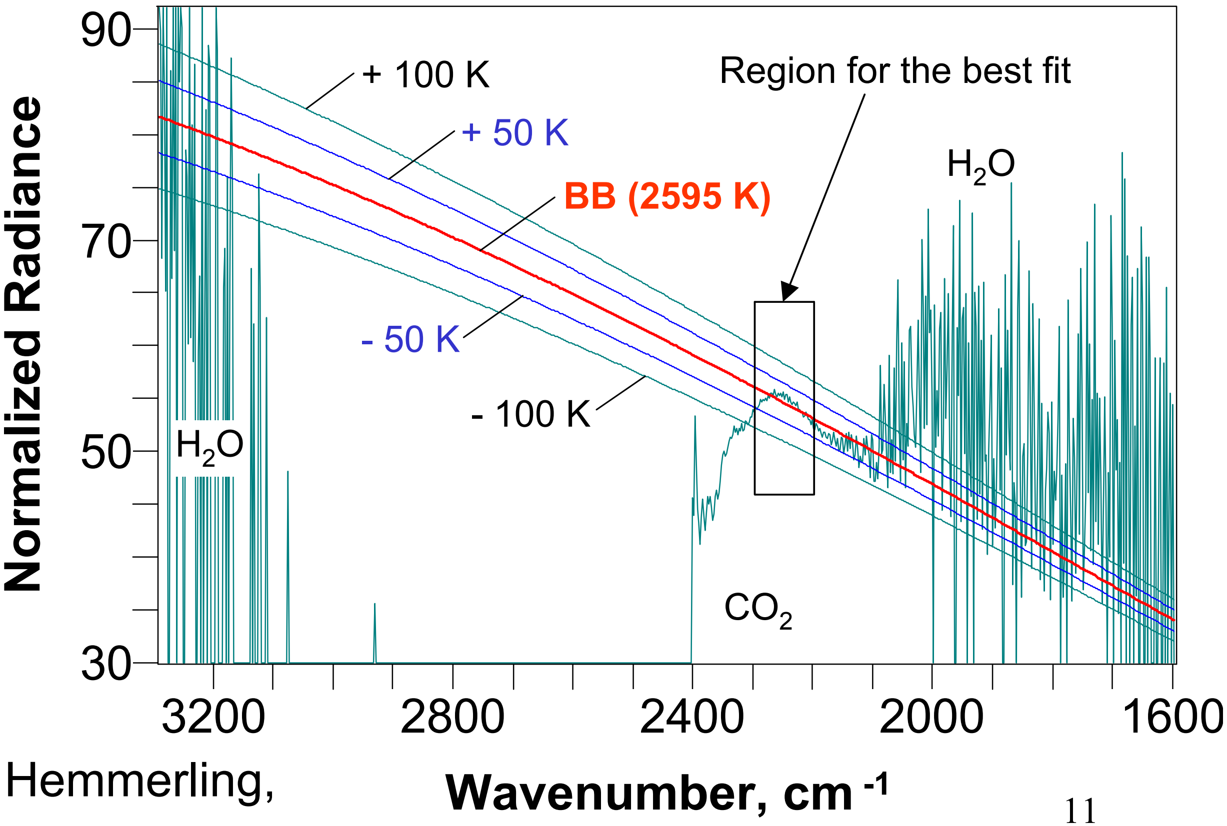
Kammler et al. (2002)
Combust. *Flame* **128**
369-381.

Determination of flame temperature and species conversion by *in situ* FTIR



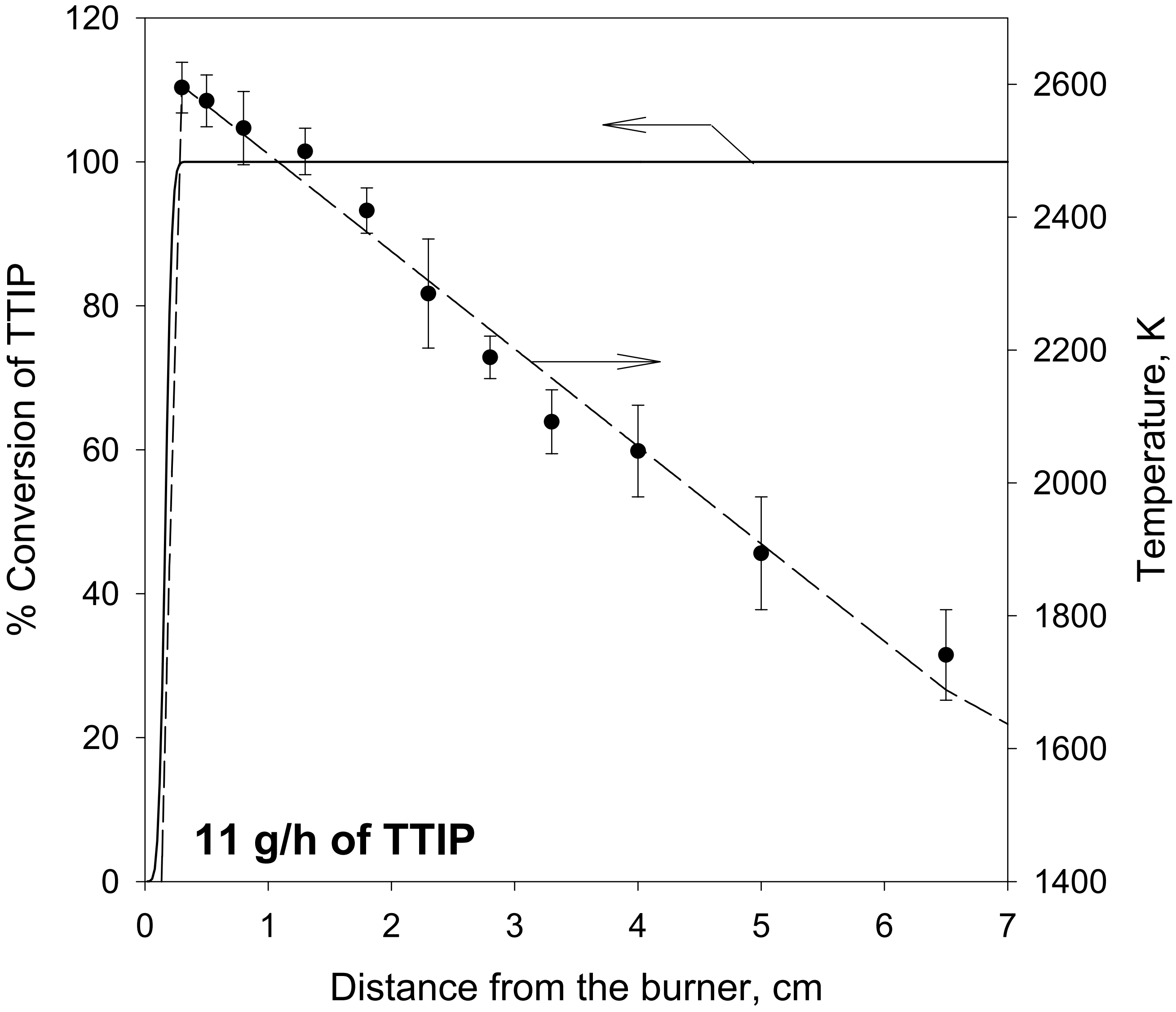
$$\text{Normalized Radiance} = \frac{\text{Radiance}(\nu,T)}{1 - \text{Transmittance}(\nu)}$$

Best, Chien, Carangelo, Solomon, Danchak, Ilovivi, *Combust. Flame* **85** (1991).



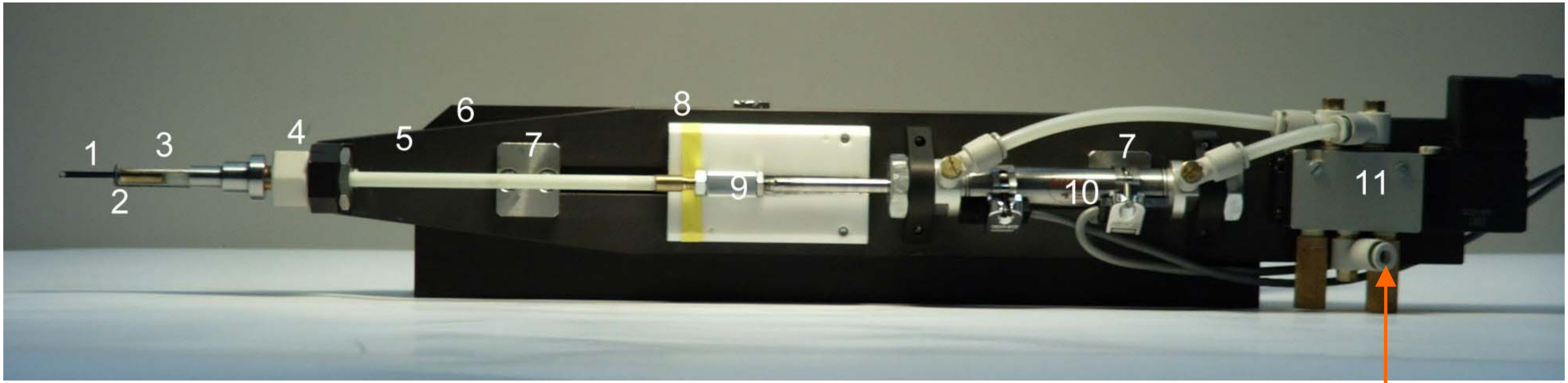
Kammler, Pratsinis, Morrison, Hemmerling, *Combust. Flame* **128** (2002).

Temperature Profile and Precursor Conversion

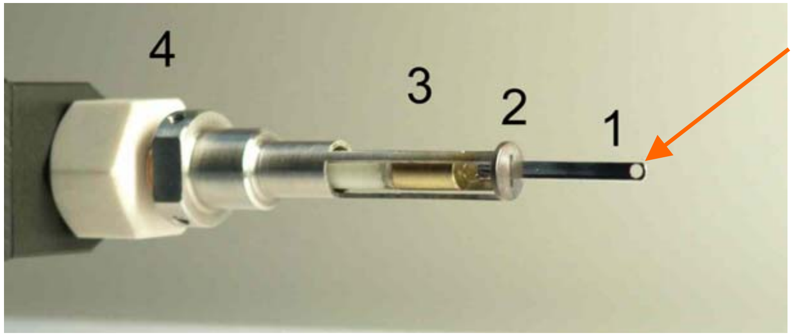


Thermophoretic particle sampler

(original design by Dobbins and Megaridis, 1987)



5 bar N_2 pressure

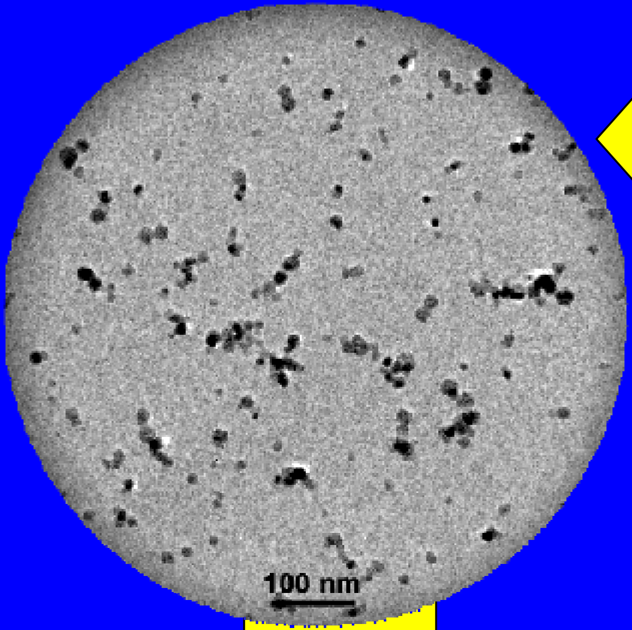


TEM grid

t_{res} = 50 ms

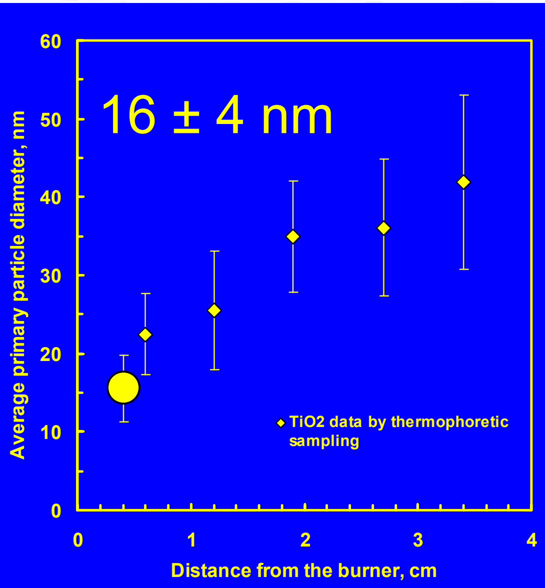
Synthesis of Nanoparticles in Flame Aerosol Reactors

Thermophoretic Sampling (Height: 0.3 cm)



TEM

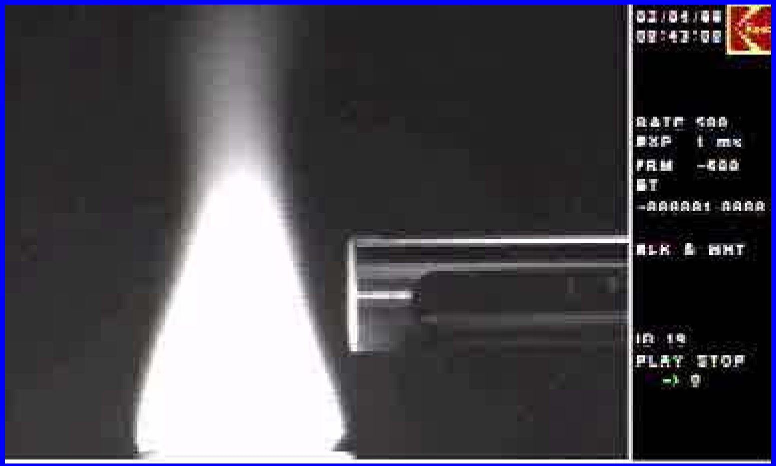
Image Analysis



Eidgenössische Technische Hochschule Zürich

Synthesis of Nanoparticles in Flame Aerosol Reactors

Thermophoretic Sampling (Height: 1.1 cm)



TEM

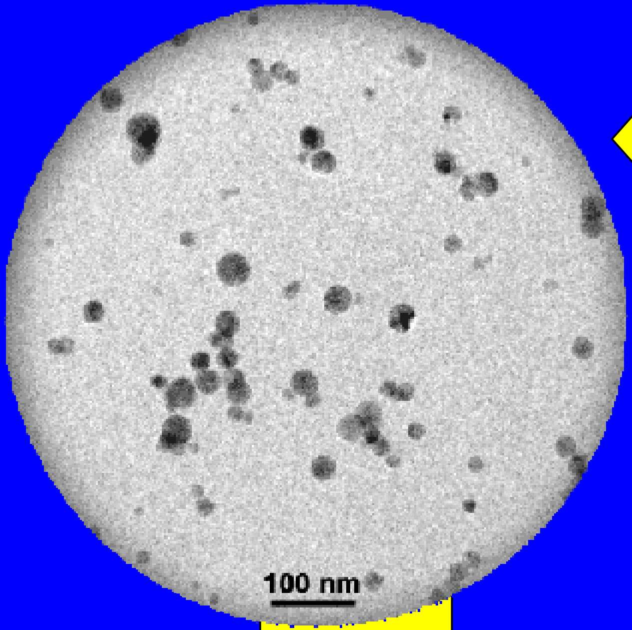
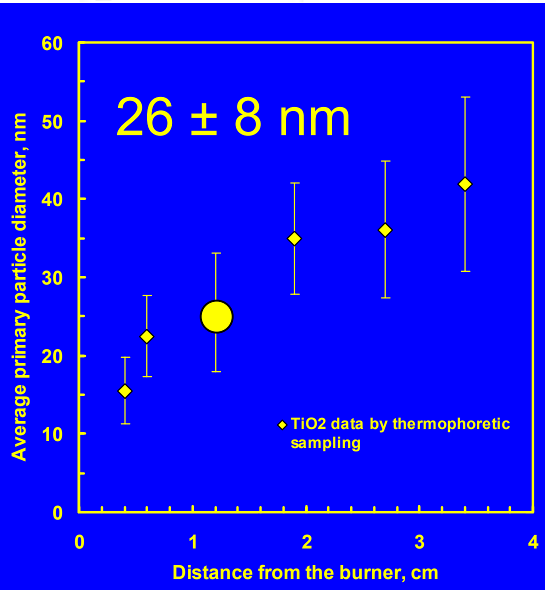


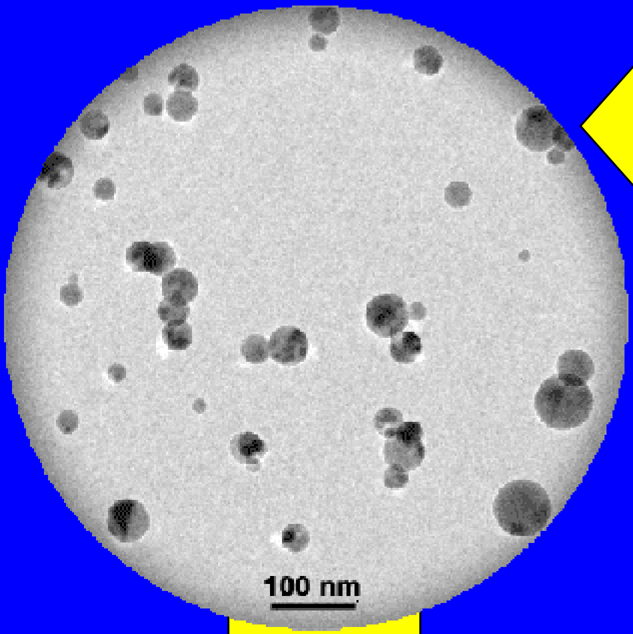
Image Analysis



Eidgenössische Technische Hochschule Zürich

Synthesis of Nanoparticles in Flame Aerosol Reactors

Thermophoretic Sampling (Height: 3.3 cm)



TEM

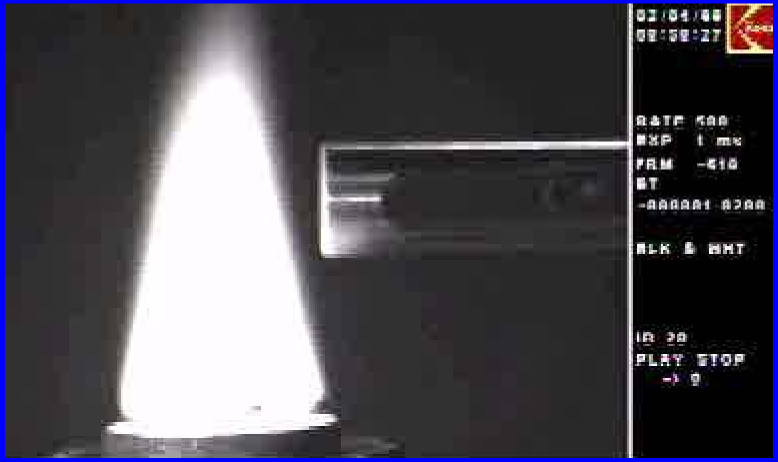
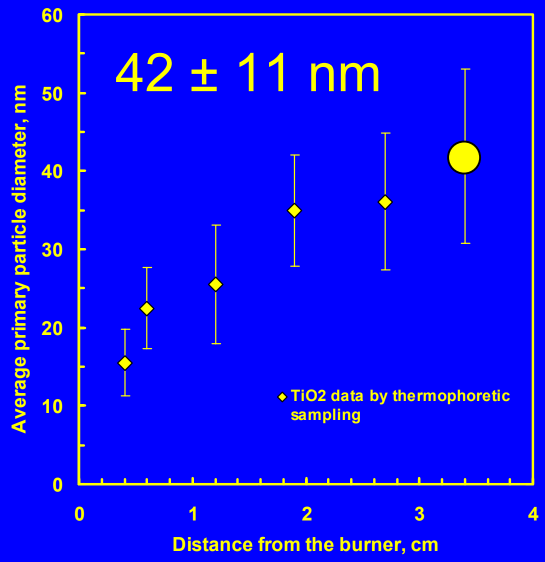


Image Analysis



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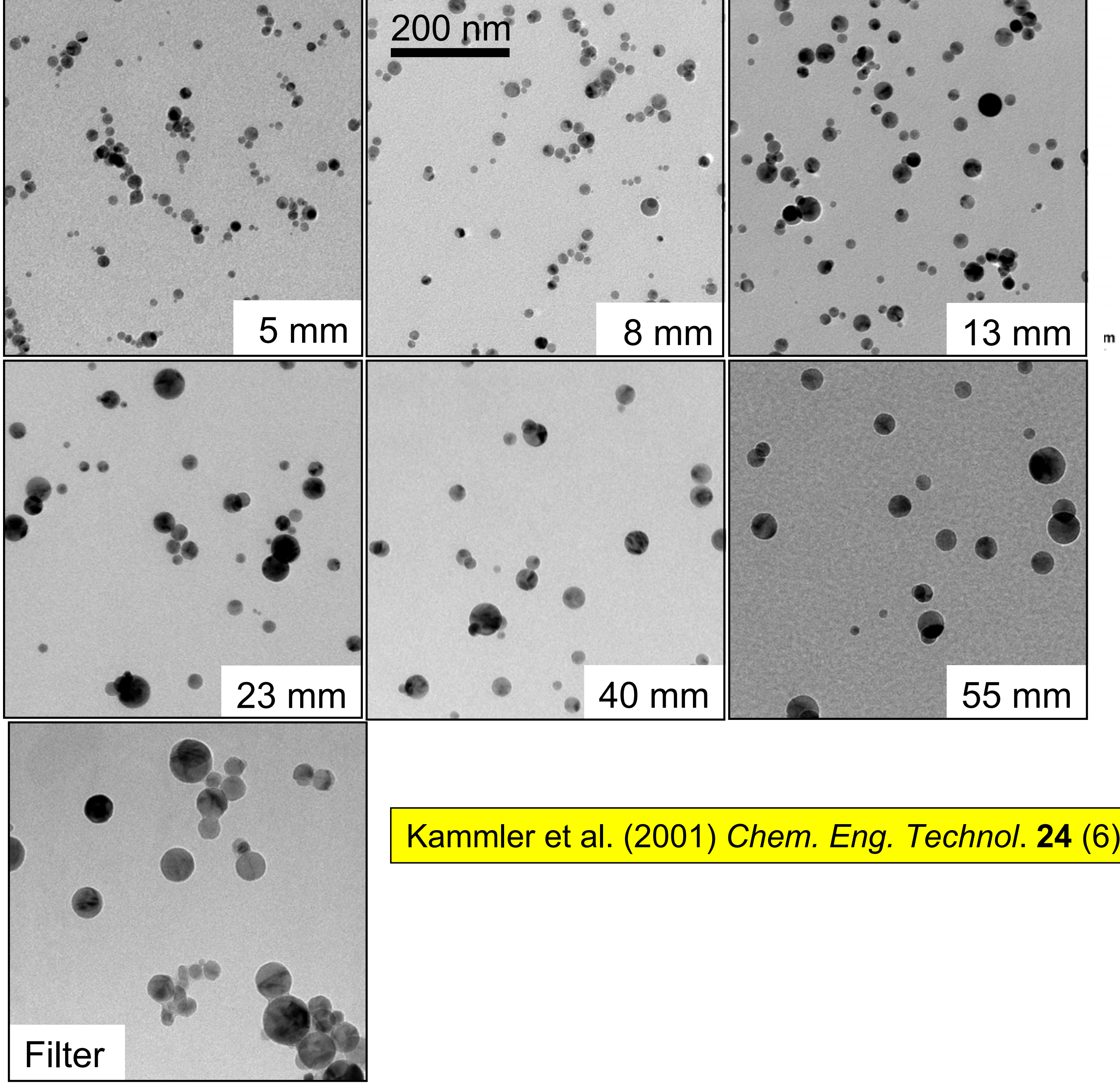
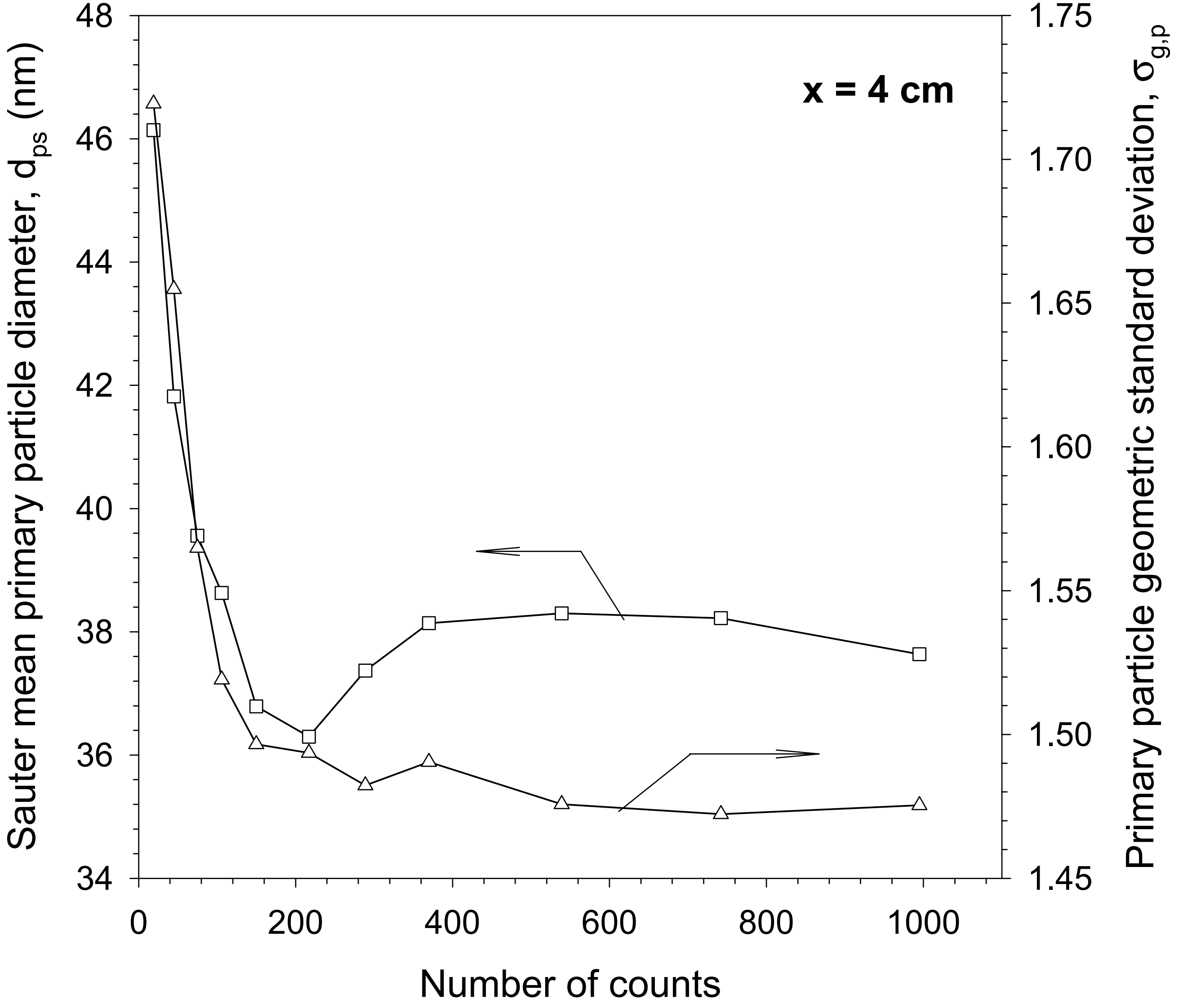
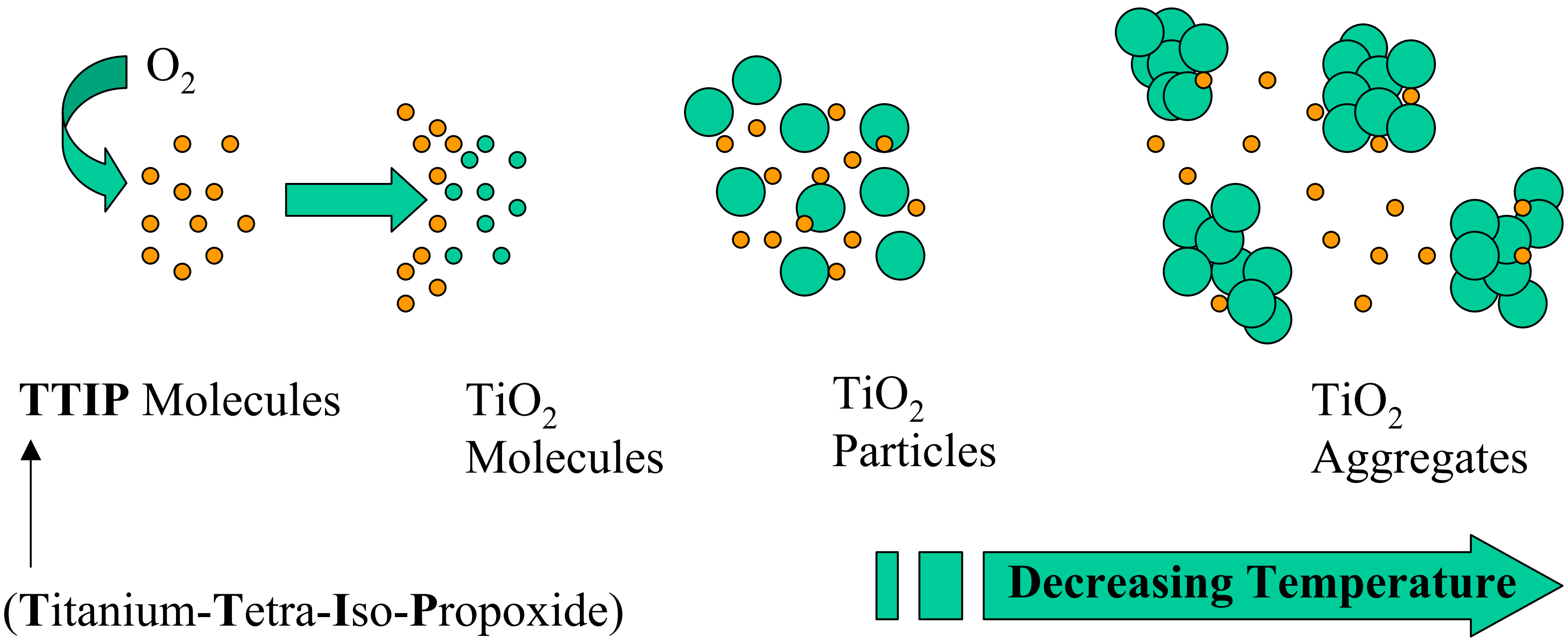


Kammler et al. (2001) *Chem. Eng. Technol*. **24** (6) 583-596

Particle Counts



Particle Formation and Growth by Gas Phase Chemical Reaction, Coagulation, Sintering and Surface Growth



TTIP Molecules

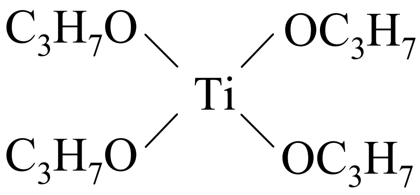
TiO_2 Molecules

TiO_2 Particles

TiO_2 Aggregates

Decreasing Temperature

(**T**itanium-**T**etra-**I**so-**P**ropoxide)



General Population Balance Equation
(in the volume space coordinate)

$$\frac{\partial n(v,t)}{\partial t} = -\frac{\partial}{\partial v}\left[g(v)n(v,t)\right] + S\delta(v - v_0) +$$

Growth & Nucleation

$$+\frac{1}{2}\int_0^v \beta(v', v - v')n(v',t)n(v - v',t)dv'$$

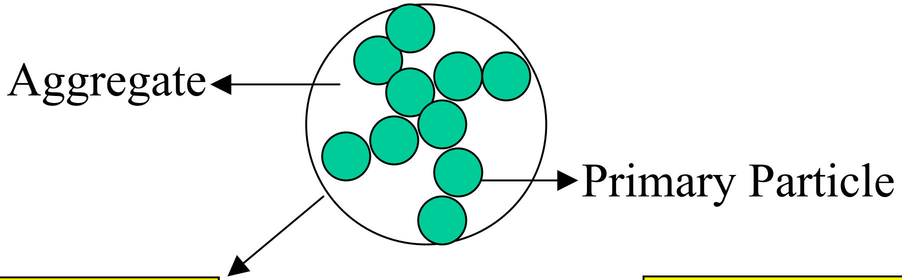
Birth by Collisions

$$-n(v,t)\int_0^\infty \beta(v, v')n(v',t)dv'$$

Death by Collisions

S. Tsantilis, H.K. Kammler and Pratsinis, S.E. *Chem. Eng. Sci.*, **57**, 2139-56 (2002).

Brownian Coagulation of Aggregates (Kruis et al., 1993)



Collision Diameter

$$d_{c,i} = d_{p,i}\left(\frac{v_i}{v_{p,i}}\right)^{1/D_f}$$

Primary Particle Diameter

$$d_{p,i} = \frac{6v_i}{\alpha_i}$$

Fuchs Coagulation Coefficient

$$\beta_{i,j} = 2\pi\left(D_i + D_j\right)\left(d_{c,i} + d_{c,j}\right)\left[\frac{d_{c,i} + d_{c,j}}{d_{c,i} + d_{c,j} + 2g_{i,j}} + \frac{8\left(D_i + D_j\right)}{c_{i,j}\left(d_{c,i} + d_{c,j}\right)}\right]^{-1}$$

Reactions and Reaction Rates

Thermal Decomposition (TD) of Titanium-Tetra-Iso-Propoxide (TTIP) (Okuyama et al., 1990)

$\mathrm{TTIP}_{(gas)} \rightarrow \mathrm{TiO_2} + 4\ \mathrm{C_3H_6} + 2\ \mathrm{H_2O}$

$k\ (1/s) = 3.96 \cdot 10^{5} \cdot \exp(-70.5\,\mathit{kJ/mol}/(R \cdot T))$

Hydrolysis (H) of Titanium-Tetra-Iso-Propoxide (TTIP) (Kashima and Sugiyama, 1990)

$\mathrm{TTIP}_{(gas)} + 2\ \mathrm{H_2O} \rightarrow \mathrm{TiO_2} + 4\ \mathrm{C_3H_7OH}$

$k\ (1/s) = 3 \cdot 10^{15} \cdot \exp(-8.43\,\mathit{kJ/mol}/(R \cdot T))$

Surface Reaction (SG) of Titanium-Tetra-Iso-Propoxide (TTIP) (Battiston et al., 1997, 1999)

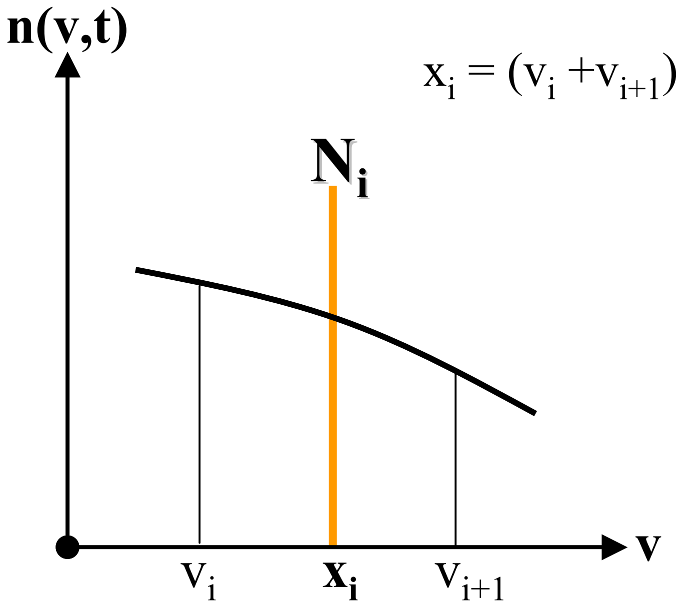
$\mathrm{TTIP}_{(surface)} \rightarrow \mathrm{TiO_2} + \ldots$

$k^{film}(cm/s) = 3 \cdot 10^{11} \cdot \exp(-126\,\mathit{kJ/mol}/(R \cdot T))$

Sectional Method of Kumar and Ramkrishna (1996)

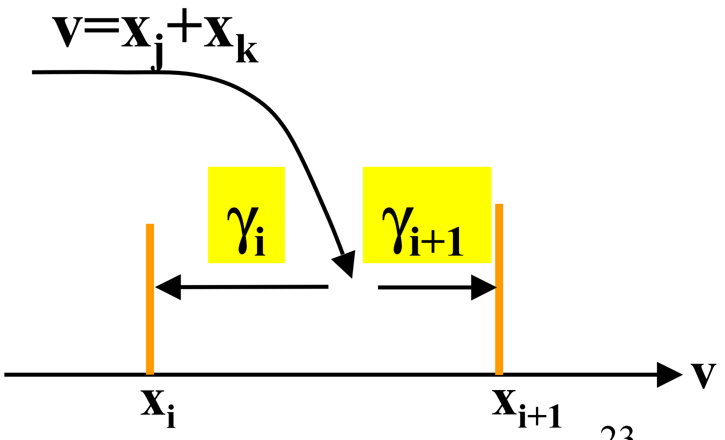
Population in *i*-th size interval is represented by a *pivot* $\mathbf{x_i}$

$$n(v,t)=\sum_{i=1}^{M} N_i(t)\delta(v-x_i)$$



Incoming particles are assigned to adjacent pivots preserving two or more moments.

$$\left\langle \begin{array}{l} \gamma_i(v,x_i)f_1(x_i)+\gamma_{i+1}(v,x_{i+1})f_1(x_{i+1})=f_1(v) \\ \gamma_i(v,x_i)f_2(x_i)+\gamma_{i+1}(v,x_{i+1})f_2(x_{i+1})=f_2(v) \end{array} \right\rangle$$



"Moving" Sectional Model for Coagulation, Surface Growth and Sintering

S. Tsantilis, H.K. Kammler and Pratsinis, S.E. *Chem. Eng. Sci.*, **57**, 2139-56 (2002).

Particle Number Concentration------------------------------

$$\frac{dN_i}{dt} = \left.\frac{dN_i}{dt}\right|_{\text{nuc}} + \left.\frac{dN_i}{dt}\right|_{\text{coag}}$$

$$\left.\frac{dN_i}{dt}\right|_{\text{coag}} = \sum_{x_{i-1}\le x_j+x_k\le x_{i+1}}^{i\ge j\ge k}\left(1-\frac{1}{2}\delta_{j,k}\right)\beta_{j,k}\left(N_jN_k\right)\gamma - \sum_{k=1}^{M}\beta_{i,k}N_iN_k$$

$$\left.\frac{dN_i}{dt}\right|_{\text{nuc}} = \left(k_gC\right)\eta_i \qquad \eta_i = \left|\begin{matrix} 1 & v_m \in \left[v_i, v_{i+1}\right] \\ 0 & v_m \notin \left[v_i, v_{i+1}\right] \end{matrix}\right. \qquad \frac{dC}{dt} = -k\cdot C$$

Particle Area Concentration----------

$$\frac{dA_i}{dt} = \left.\frac{dA_i}{dt}\right|_{\text{coag}} + \left.\frac{dA_i}{dt}\right|_{\text{sint}} + \left.\frac{dA_i}{dt}\right|_{\text{surf}} + \left.\frac{dA_i}{dt}\right|_{\text{nuc}}$$

$$\left.\frac{dA_i}{dt}\right|_{\text{coag}} = \sum_{x_{i-1}\le x_j+x_k\le x_{i+1}}^{i\ge j\ge k}\left(1-\frac{1}{2}\delta_{j,k}\right)\beta_{j,k}\left(N_jA_k + N_kA_j\right)\gamma' - A_i\sum_{k=1}^{M}\beta_{i,k}N_k$$

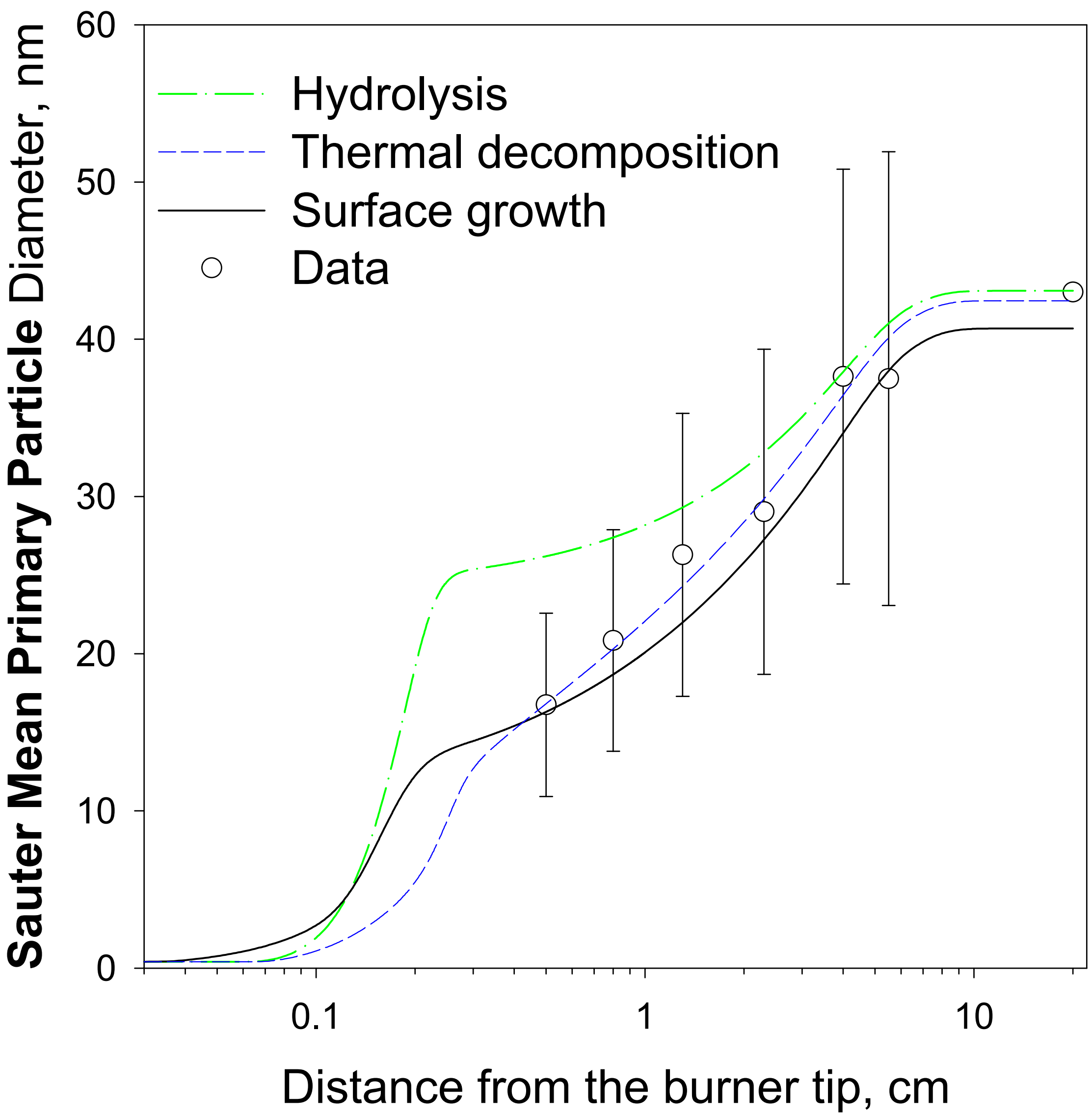
$$\left.\frac{dA_i}{dt}\right|_{\text{sint}} = -\frac{1}{\tau_{s,i}}\left(A_i - N_i\alpha_{i,s}\right) \qquad \left.\frac{dA_i}{dt}\right|_{\text{surf}} = 4\pi N_i n_{p,i} k_s d_{p,i} C v_m \qquad \left.\frac{dA_i}{dt}\right|_{\text{nuc}} = \left(k_gC\right)\alpha_m\eta_i$$

Particle Volume at the representative point (pivot)-----------------

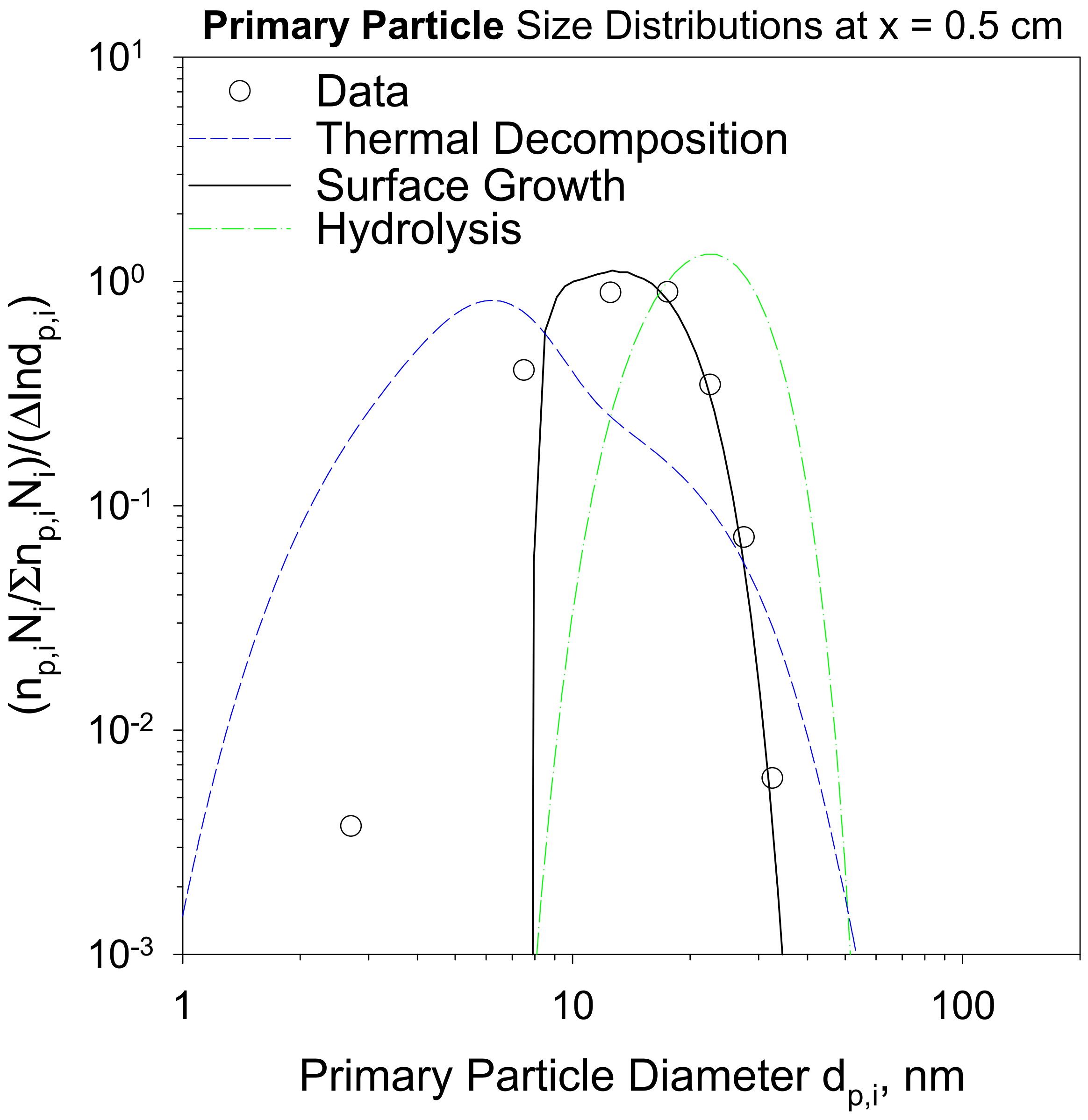
$$\frac{dx_i}{dt} = \left.\frac{dx_i}{dt}\right|_{\text{nuc}} + \left.\frac{dx_i}{dt}\right|_{\text{surf}}$$

$$\left.\frac{dx_i}{dt}\right|_{\text{surf}} = \frac{k_sCA_iv_m}{N_i} \qquad \left.\frac{dx_i}{dt}\right|_{\text{nuc}} = \frac{1}{N_i}\left(v_m - x_i\right)\left(k_gC\right)\eta_i$$

Simulation Results and Comparison with Experimental Data

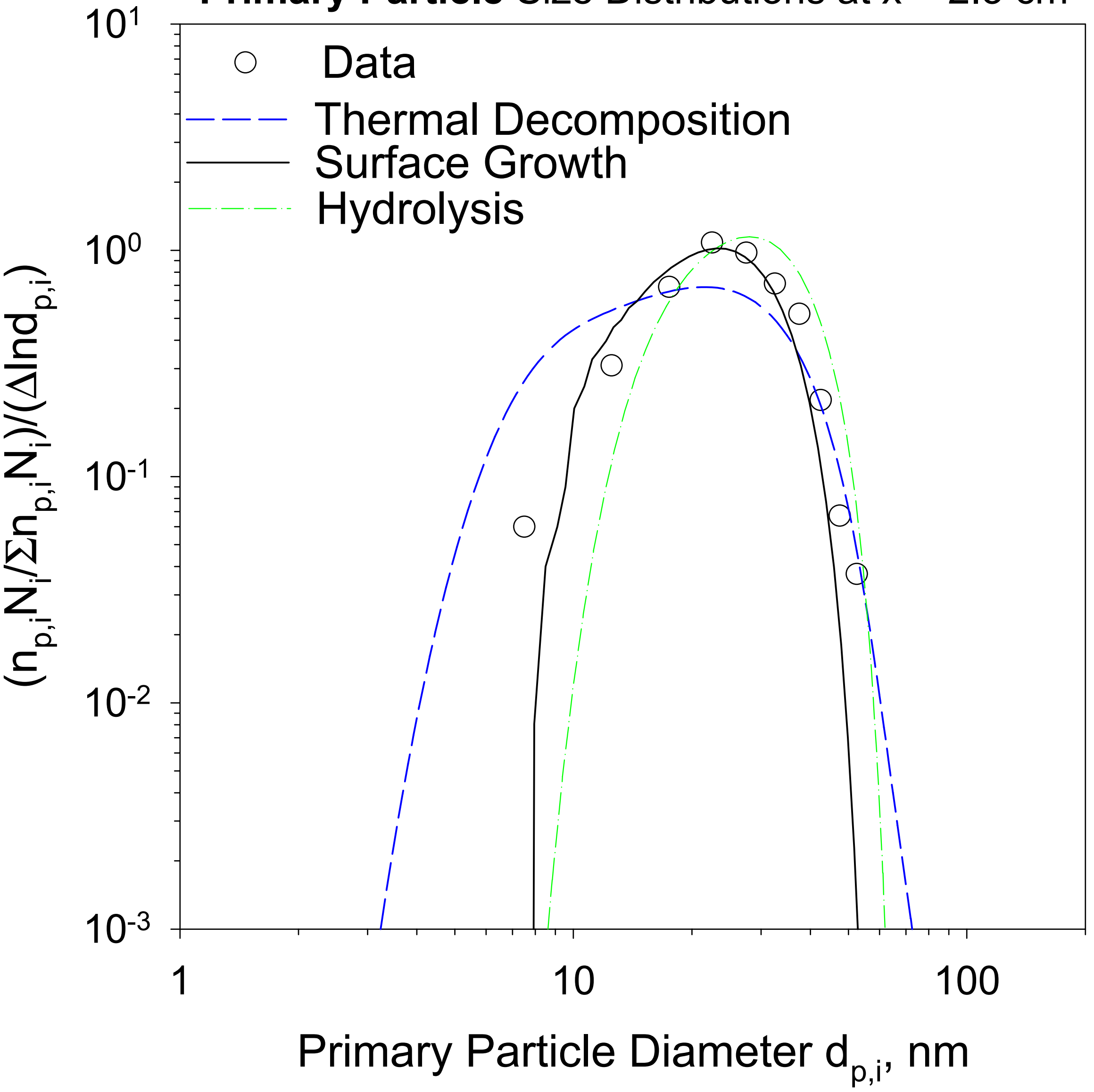


Simulation Results and Comparison with Experimental Data

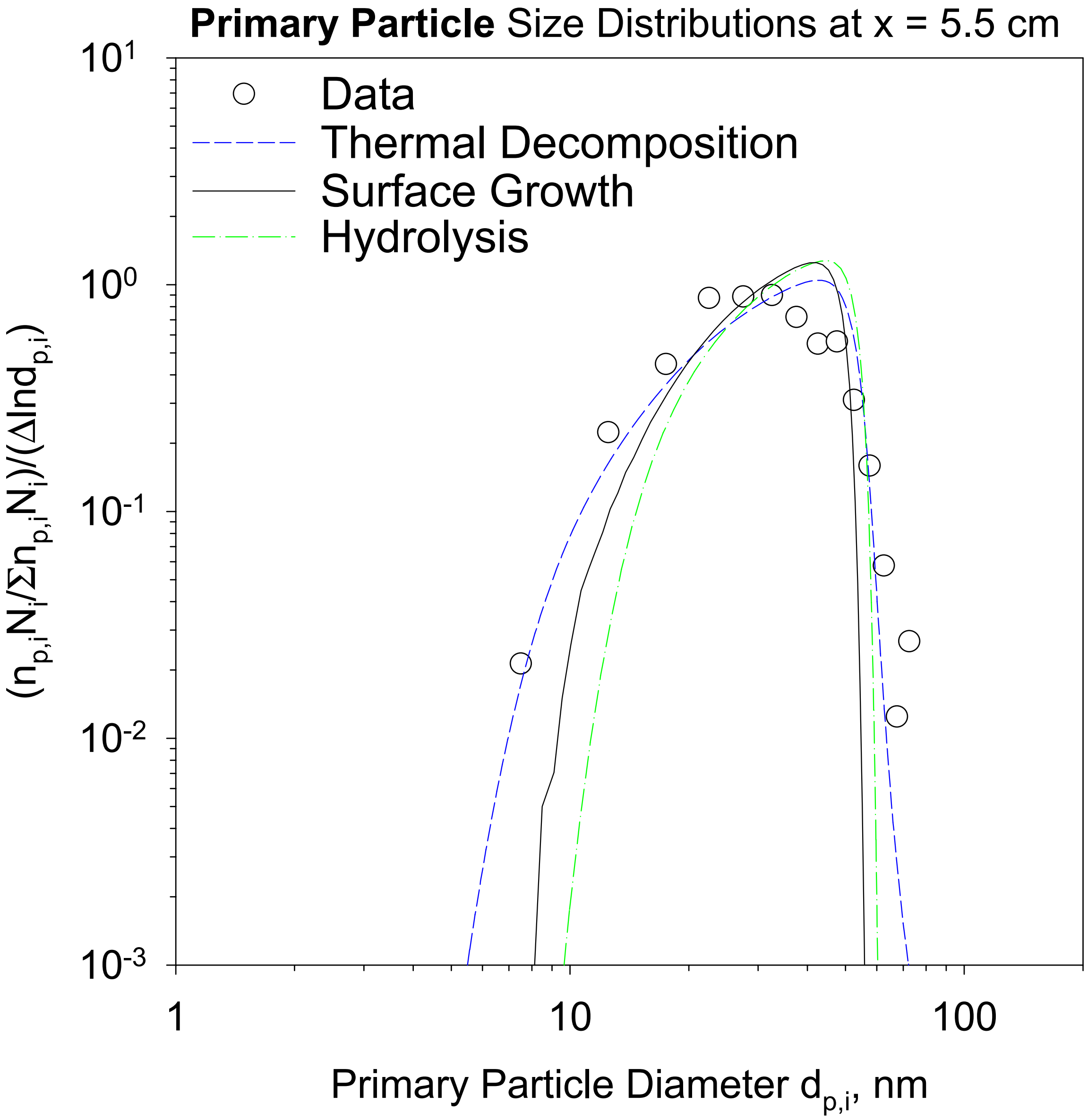


S. Tsantilis, H.K. Kammler and Pratsinis, S.E. *Chem. Eng. Sci.*, **57**, 2139-56 (2002).

Primary Particle Size Distributions at x = 2.3 cm



S. Tsantilis, H.K. Kammler and Pratsinis, S.E. *Chem. Eng. Sci.*, **57**, 2139-56 (2002).



Monodisperse model for coagulation, sintering and surface growth

S. Tsantilis, H.K. Kammler and Pratsinis, S.E. *Chem. Eng. Sci.*, **57**, 2139-56 (2002).

Precursor Concentration

$$\frac{dC}{dt} = kC = \left(k_g + k_s A\right)C$$

Total Number Concentration

$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2 + k_g C$$

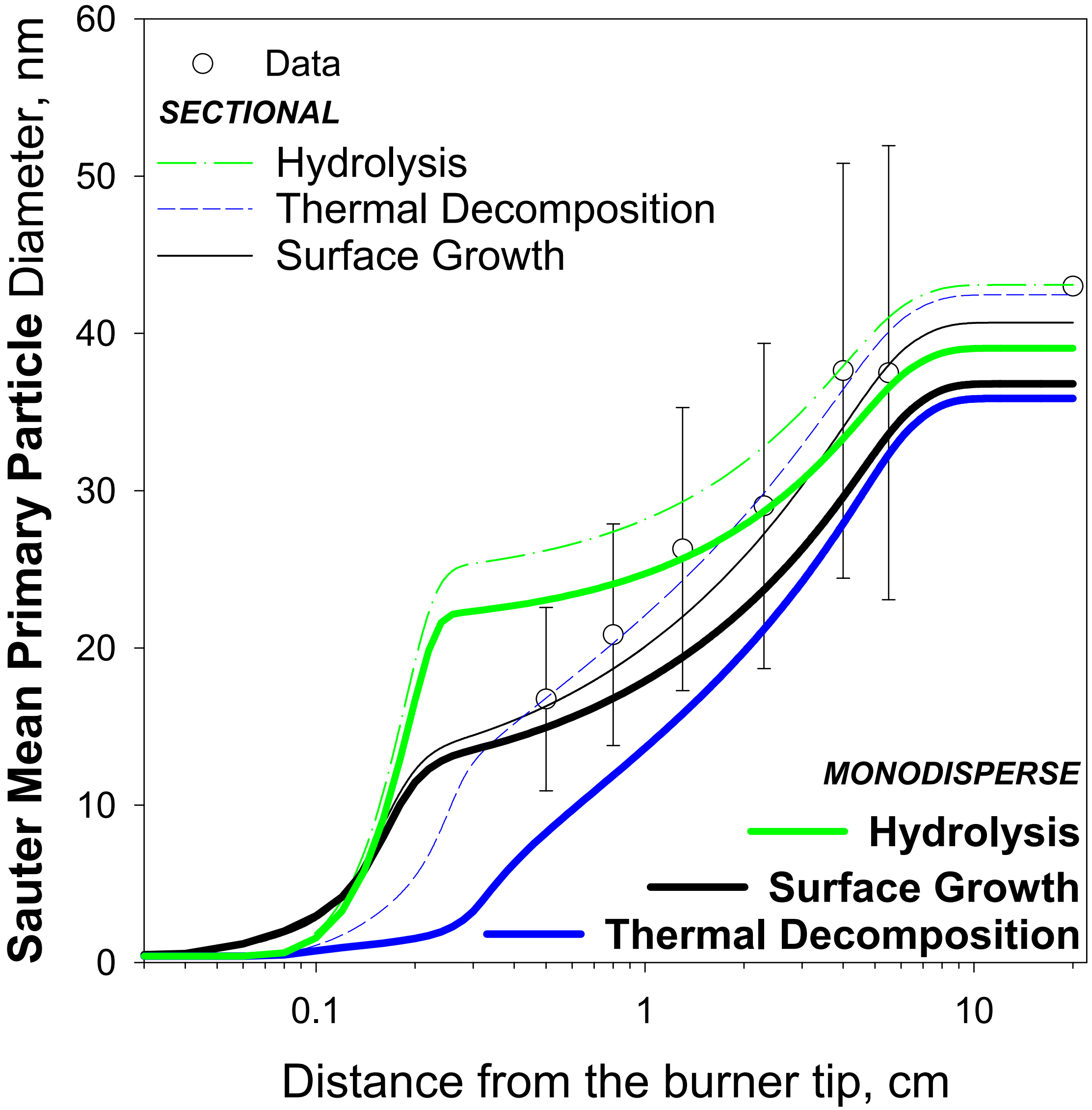
Total Surface Area Concentration

$$\frac{dA}{dt} = k_g C\alpha_m - \frac{1}{\tau_s}(A - N\cdot\alpha_s) + 4\pi N n_P d_p (k_s C) v_m$$

Total Volume Concentration

$$\frac{dV}{dt} = kCv_m$$

Sectional versus Monodisperse Simulation Results



Conclusions 1

- ☑ Chemistry determines size characteristics of nanoparticles made in flames in contrast to the dominance of self-preserving theory for larger ones.
- ☑ Surface reaction dominates early particle formation and growth.
- ☑ Molecular dynamics can contribute greatly to nanoparticle formation
- ☑ Monodisperse predictions are close to sectional calculations (20% w.r.t. dp).

Reactor Design by Computational Fluid & Particle Dynamics

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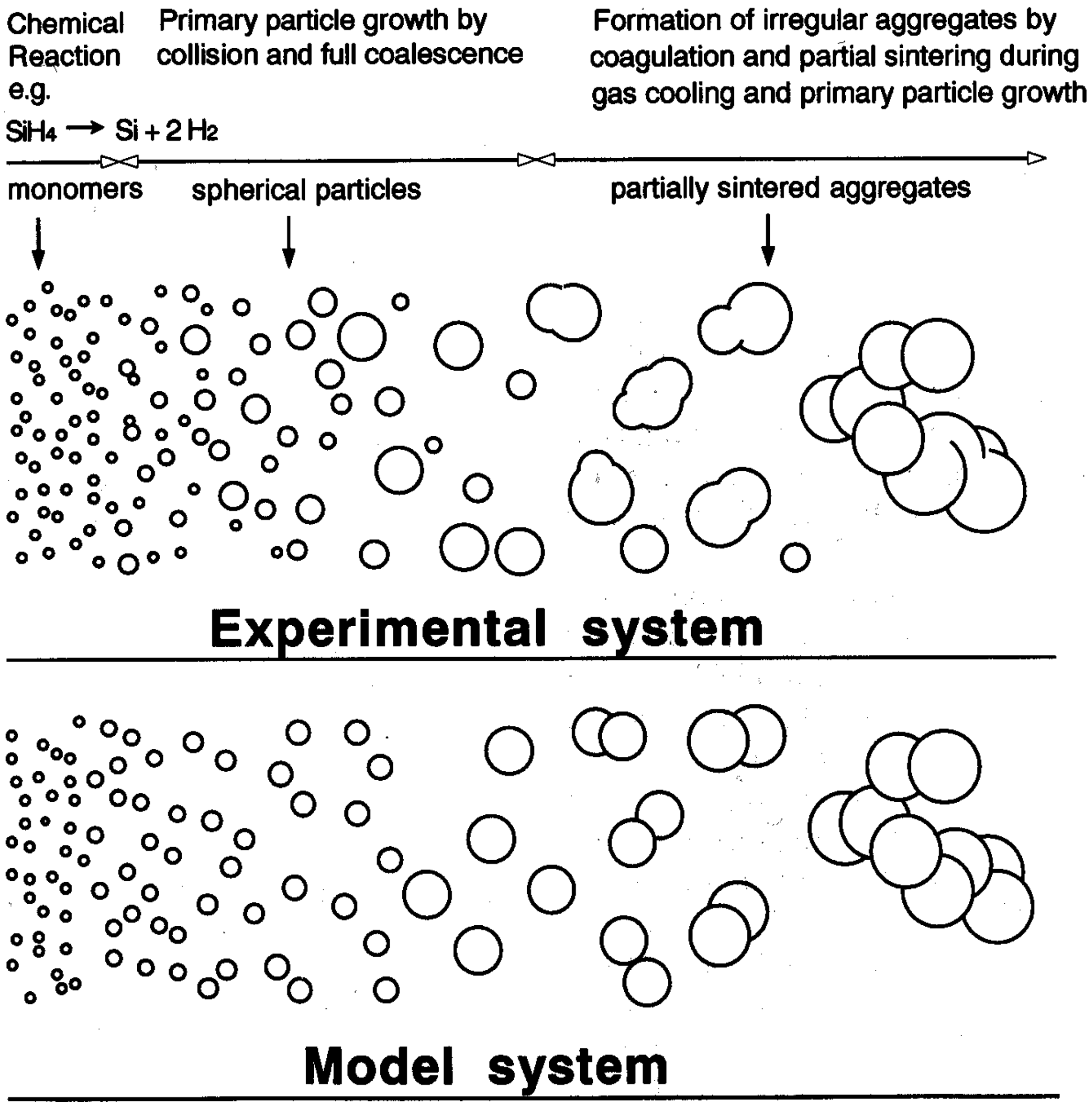
Sintering rate of particle area a

$$\frac{da}{dt} = -\frac{1}{\tau}(a - a_s)$$

Koch, Friedlander, *J. Colloid Interface Sci.* **140**, 419 (1990)

Simple model



$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2$$

$$\frac{da}{dt} = -\frac{1}{N}\frac{dN}{dt}a - \frac{1}{\tau}(a - a_s)$$

$$d_c = d_p(v / v_p)^{1/D_f}$$

Kruis, Kusters, Pratsinis, Scarlett, *Aerosol Sci. Technol*. **19**, 514 (1993)

Einbinden der Populationsbilanzen

Kollision:

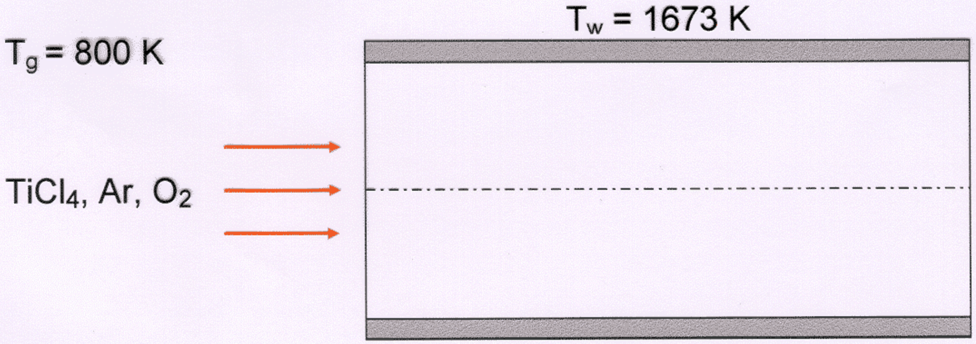
$$\frac{dN}{dt} = -\frac{1}{2} \cdot \beta \cdot N^2 \longrightarrow \frac{\partial(\rho_g u_k N)}{\partial x_k} = -\left[\frac{1}{2} \cdot \beta \cdot \rho_g{}^2 \cdot N\right] \cdot N + I$$

Sintern:

$$\frac{da}{dt} = -\frac{1}{N} \cdot \frac{dN}{dt} \cdot a - \frac{1}{\tau} \cdot (a - a_s) \longrightarrow \frac{\partial(\rho_g u_k A)}{\partial x_k} = -\left[\frac{\rho_g}{\tau}\right] \cdot A + \frac{\rho_g}{\tau} \cdot A_s + I \cdot a_o$$

Beispiele

Vorgemischt

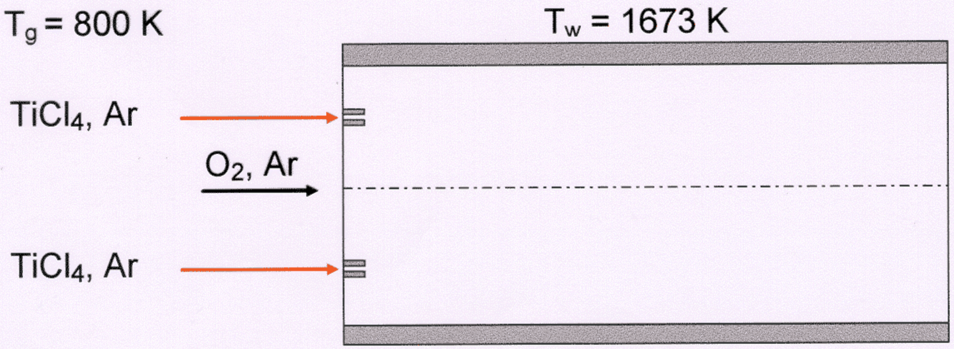


$T_g = 800$ K

$T_w = 1673$ K

$TiCl_4$, Ar, O_2

Diffusion



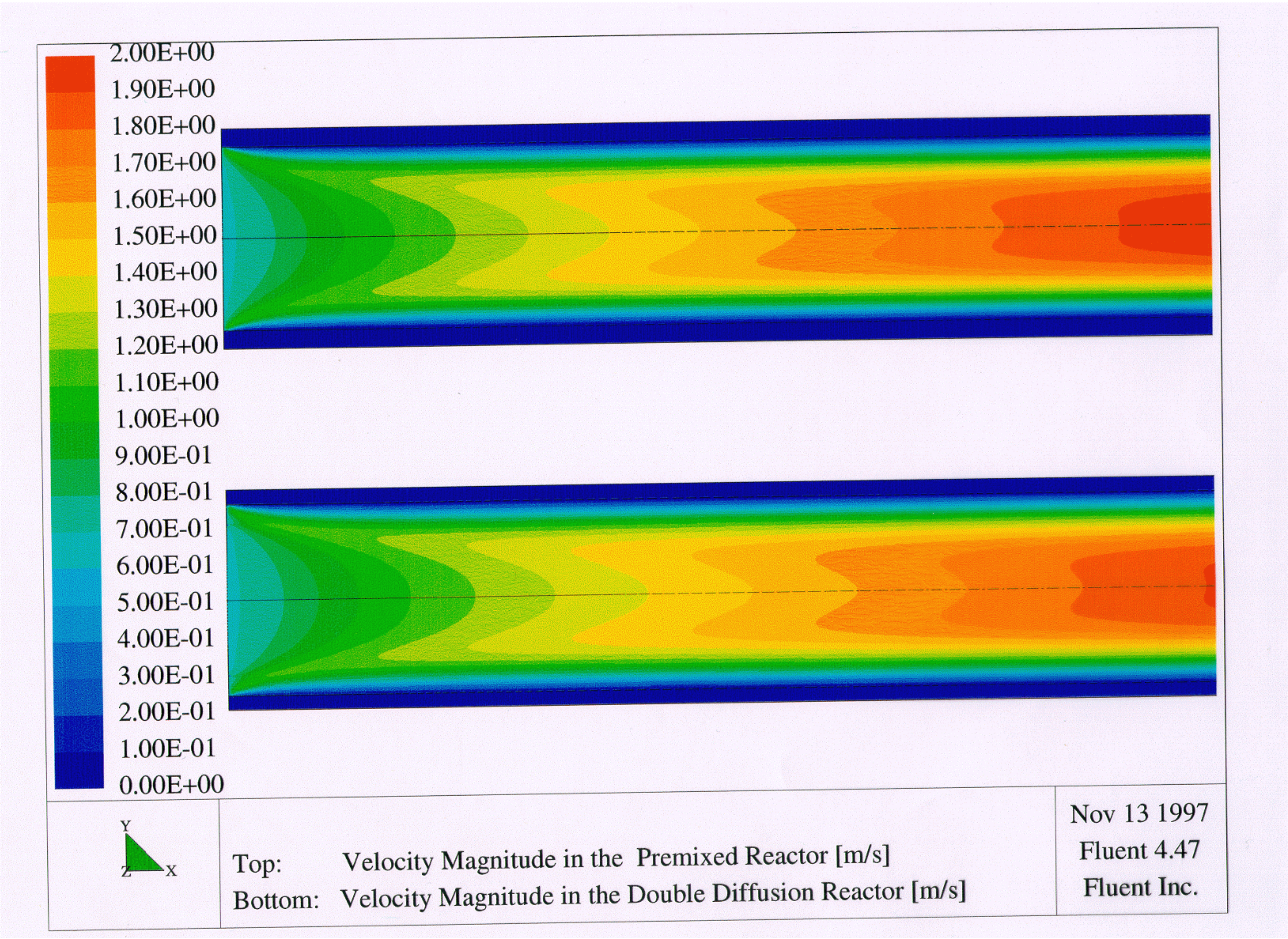
$T_g = 800$ K

$T_w = 1673$ K

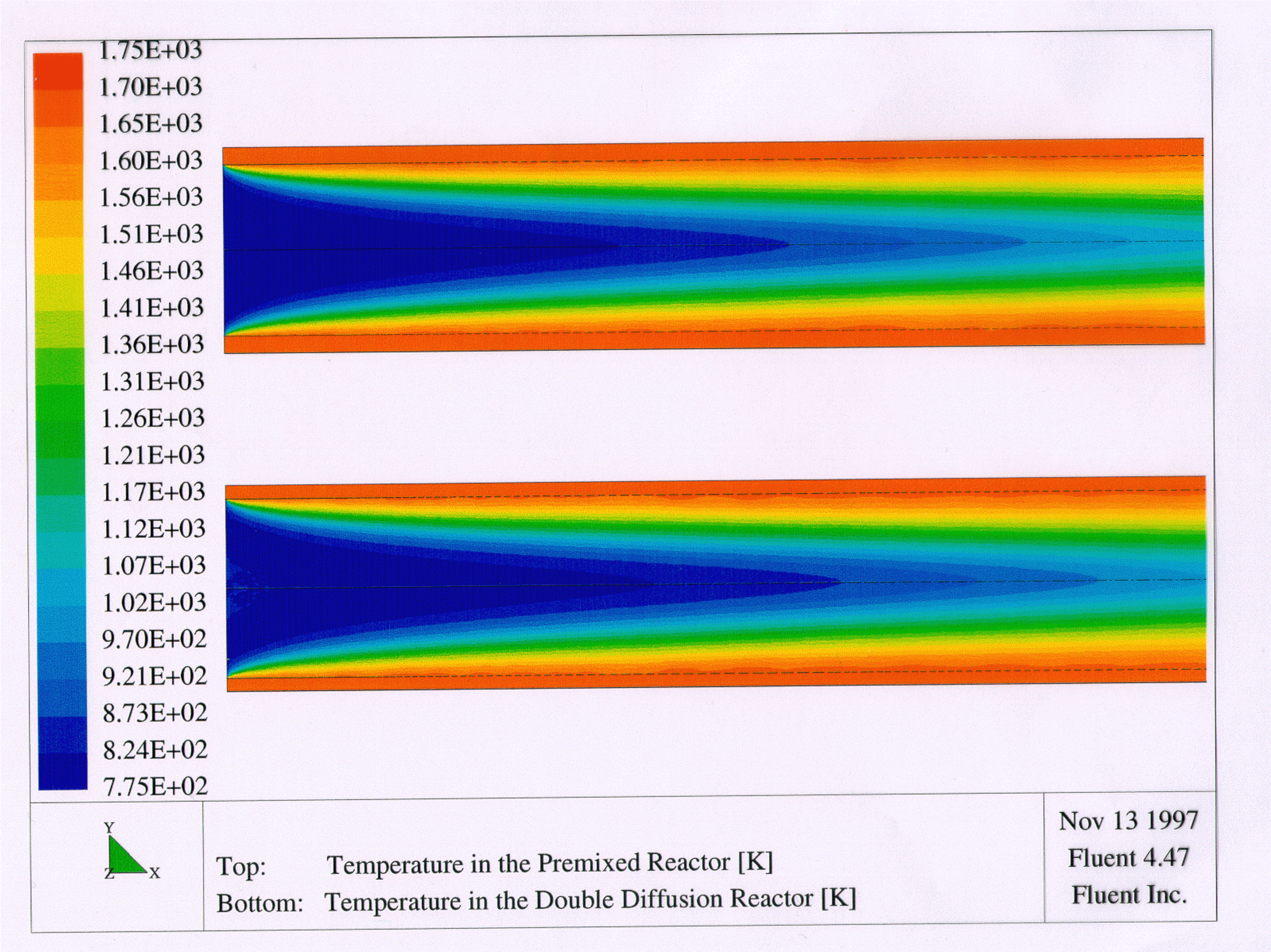
$TiCl_4$, Ar

O_2, Ar

$TiCl_4$, Ar



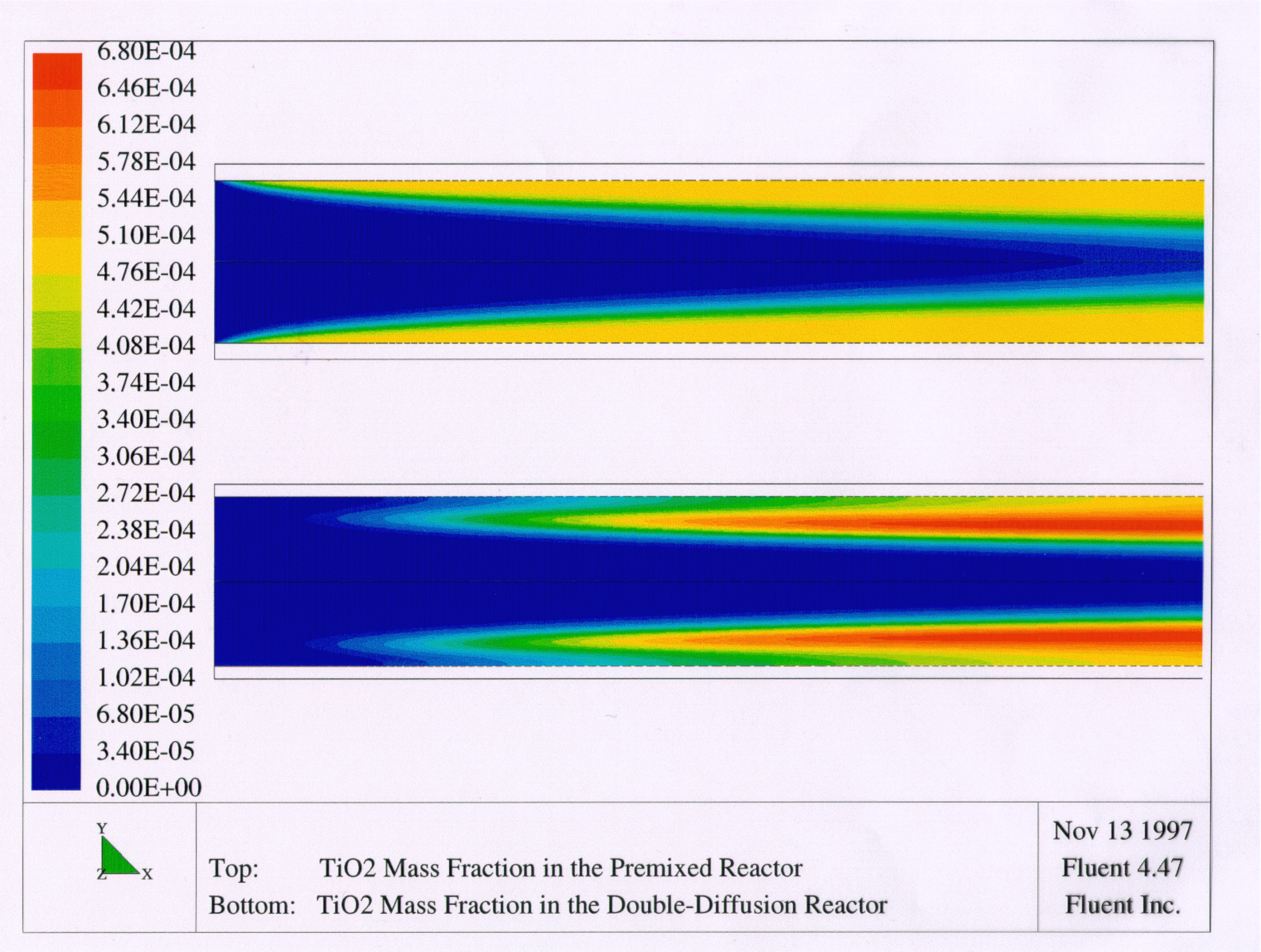
Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



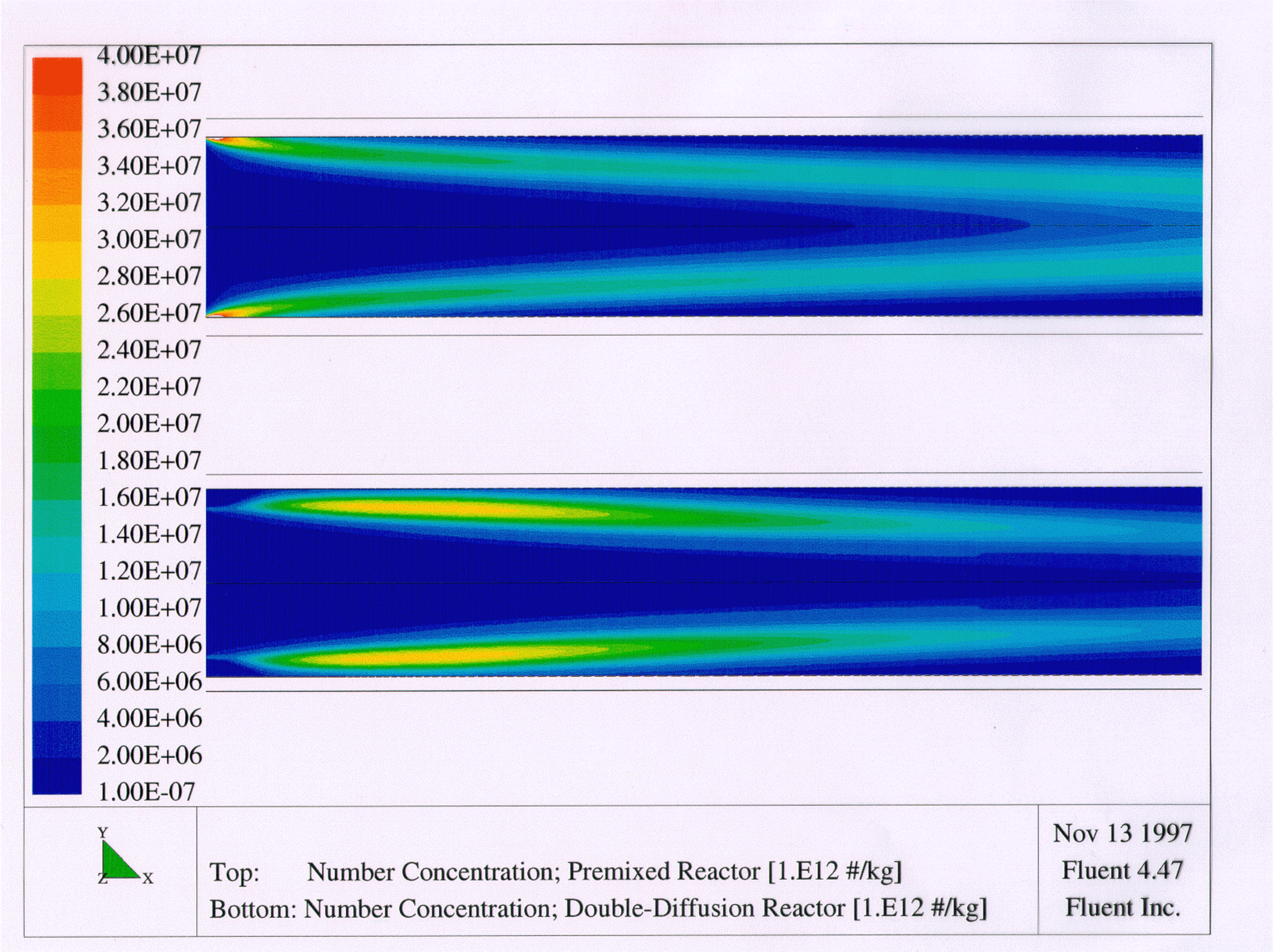
Top: Temperature in the Premixed Reactor [K]
Bottom: Temperature in the Double Diffusion Reactor [K]

Nov 13 1997
Fluent 4.47
Fluent Inc.

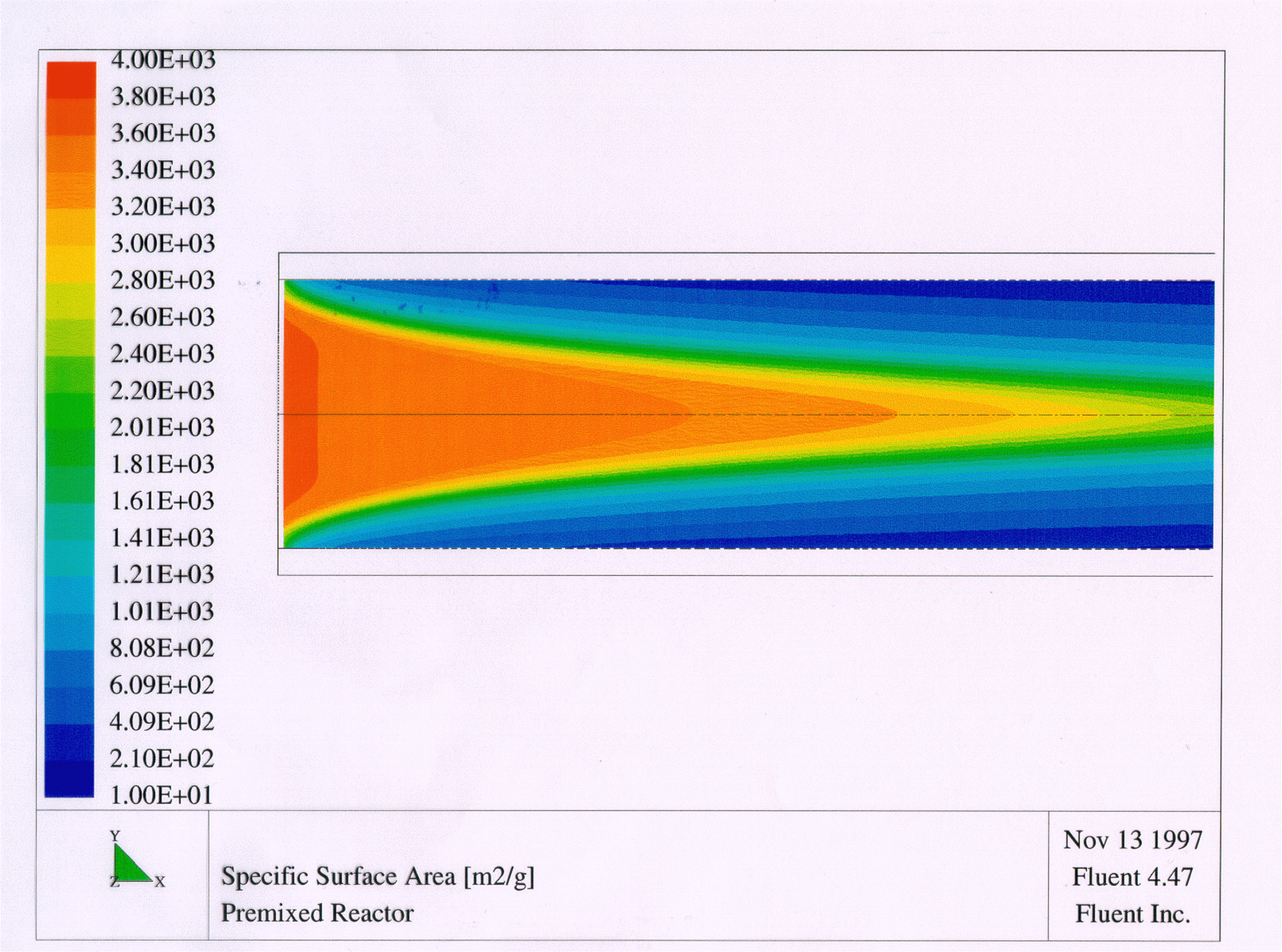
Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



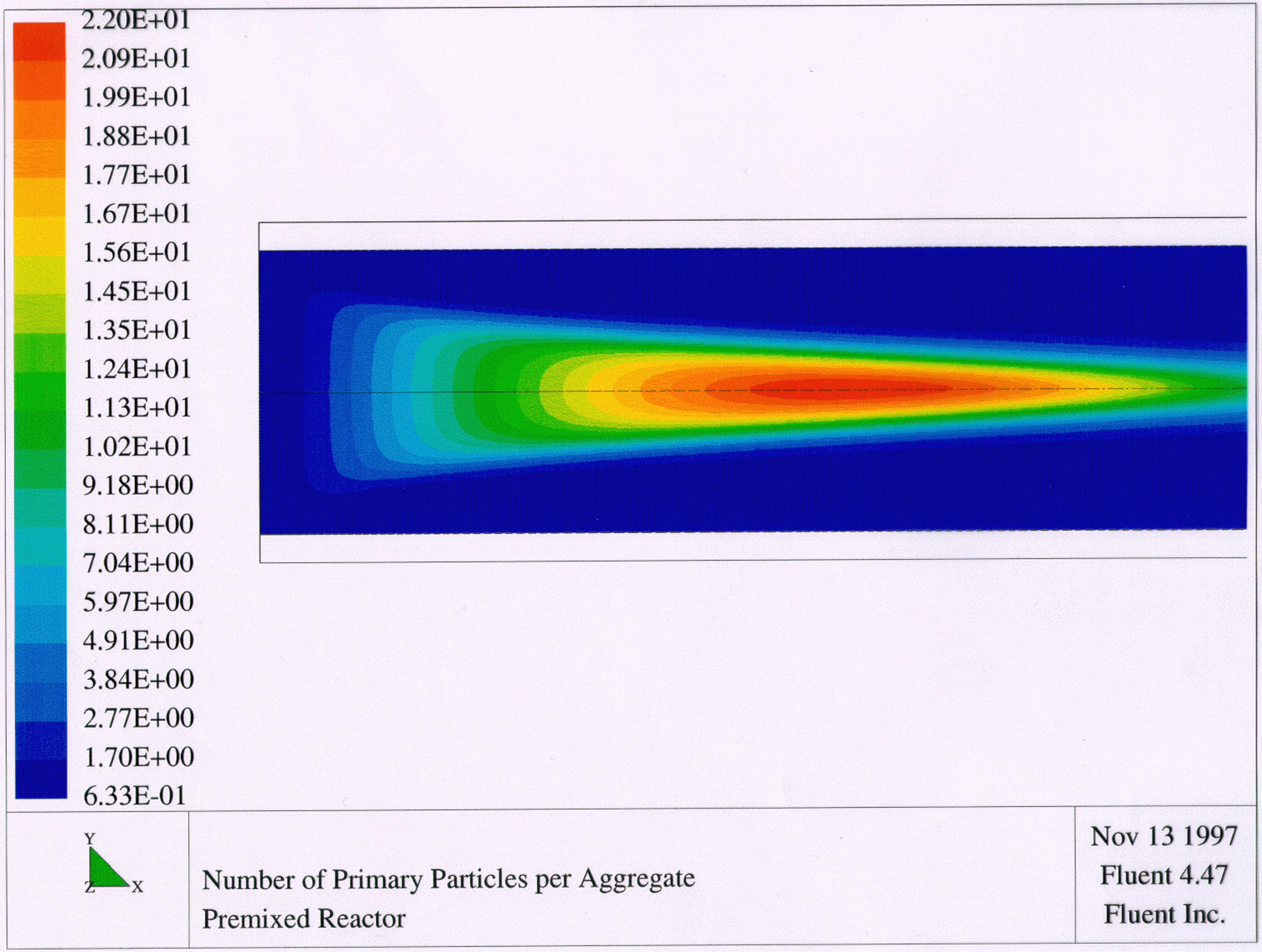
Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



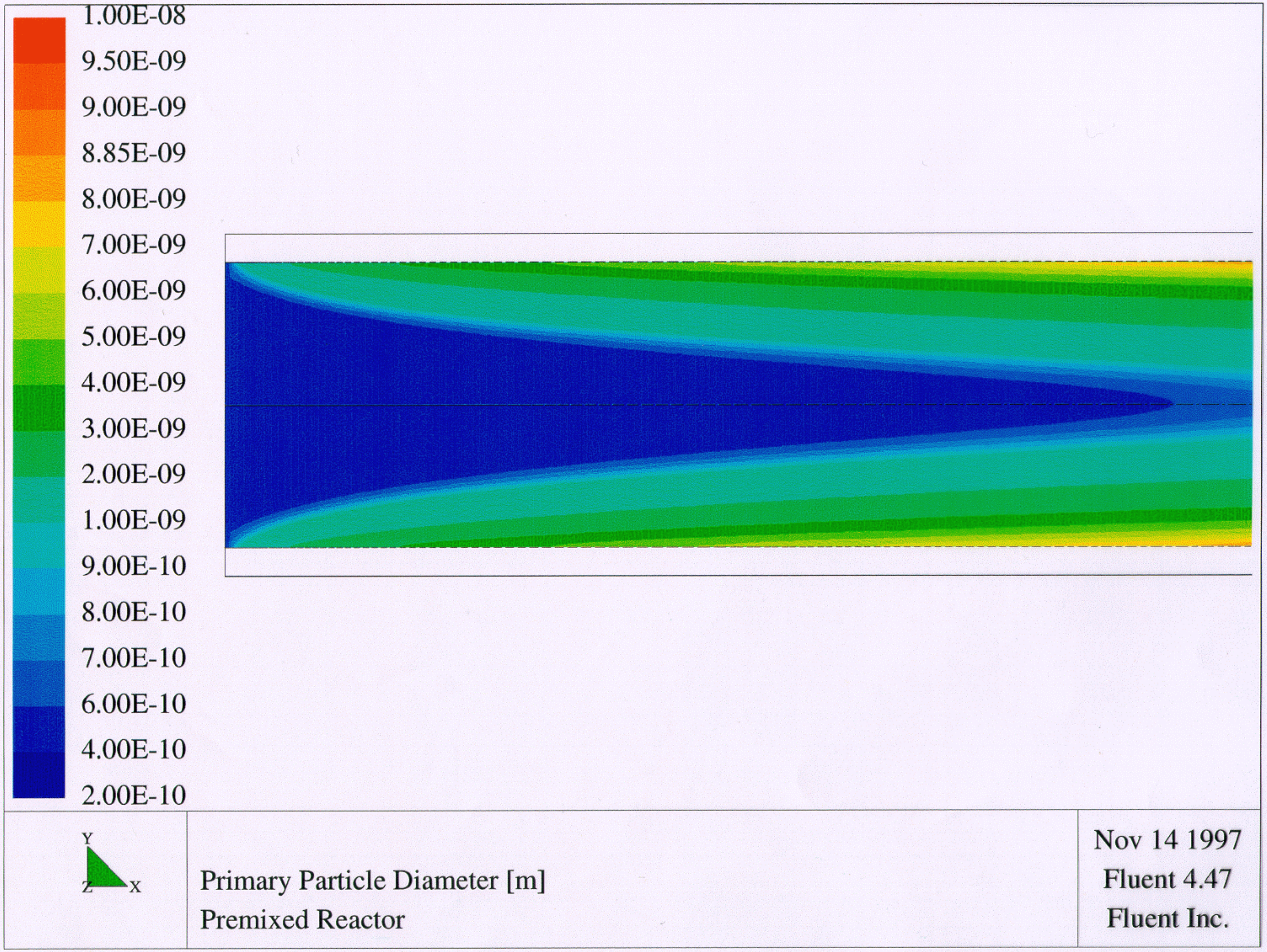
Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



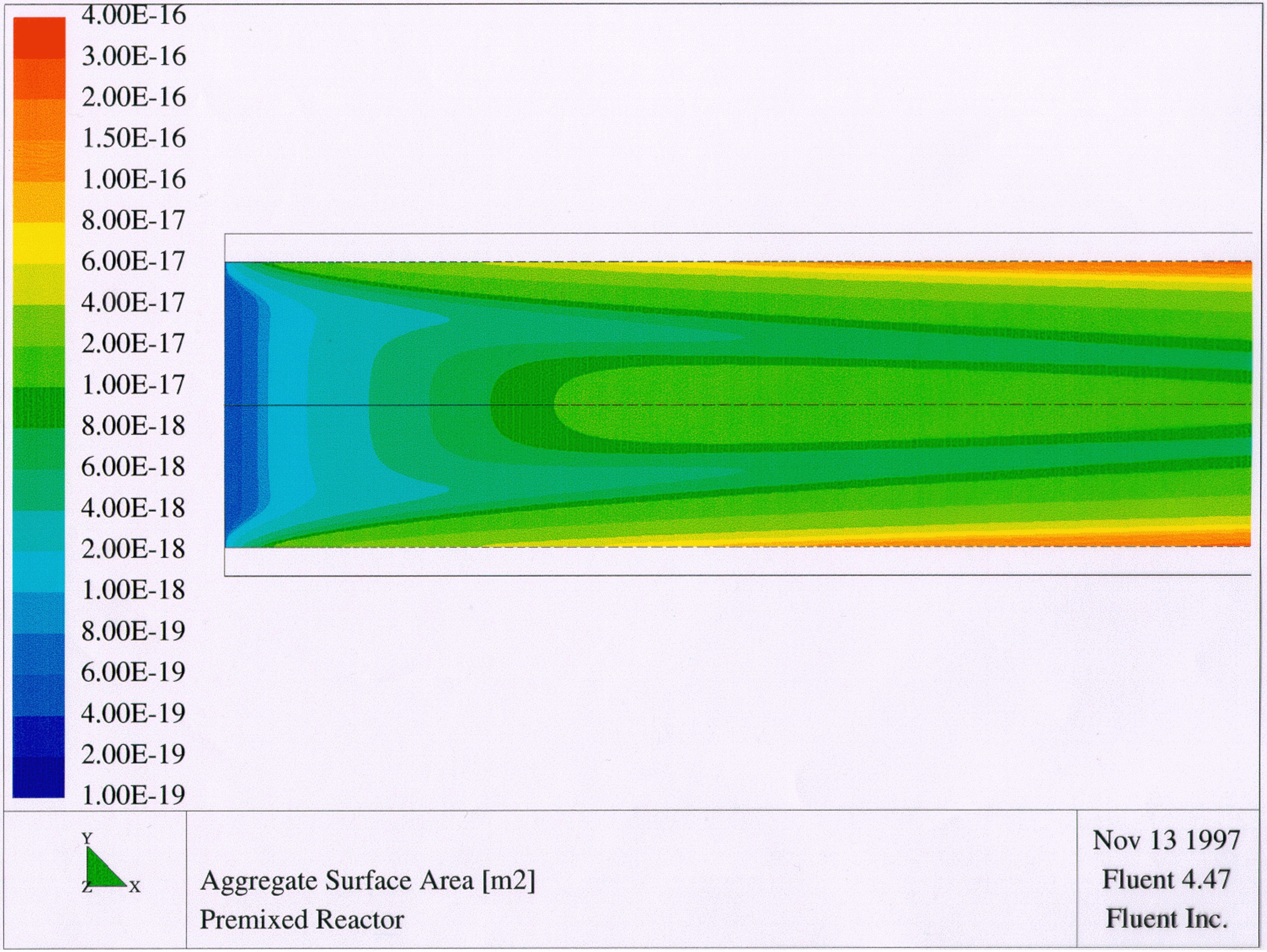
Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



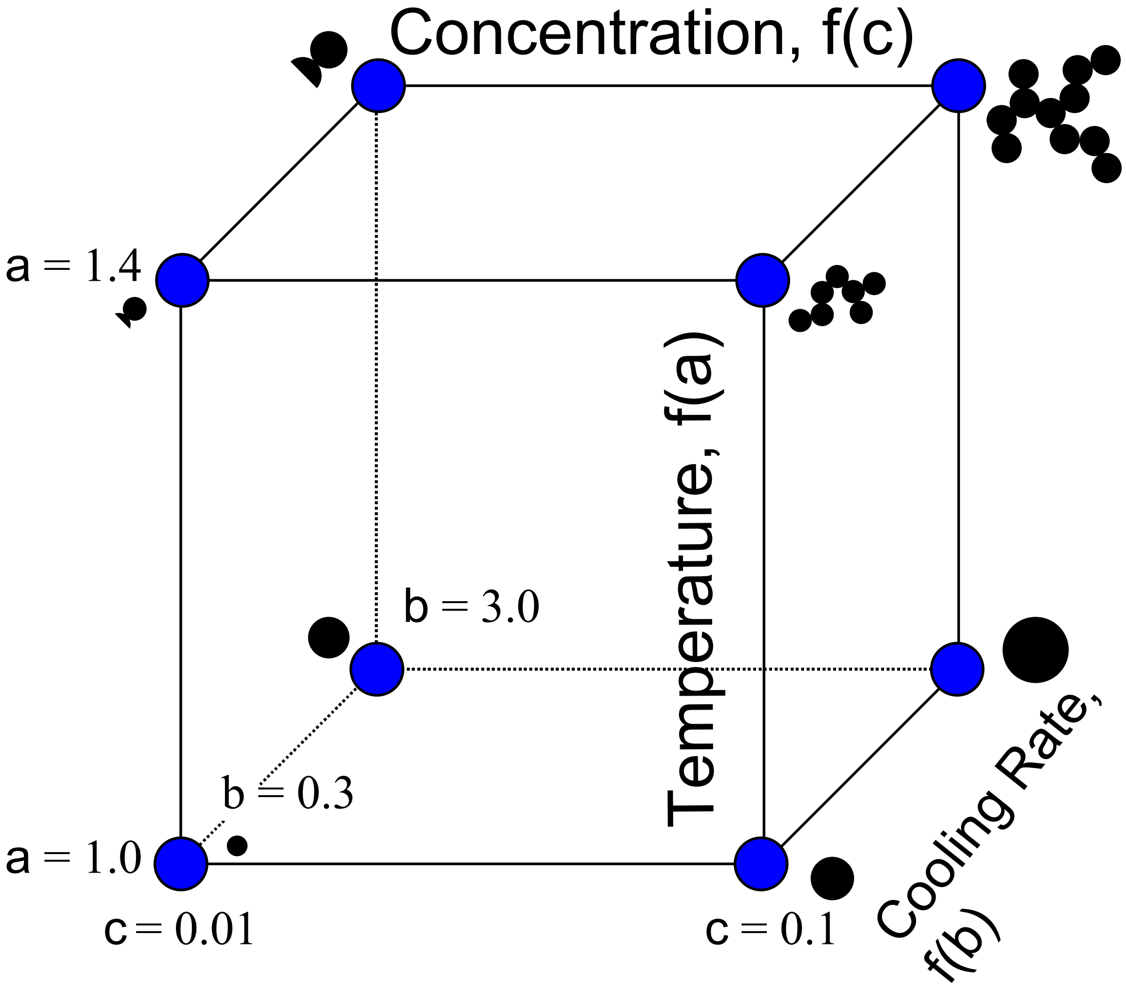
Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



Schild, Gutsch, Muhlenweg, Kerner, Pratsinis, *J. Nanoparticle Res*. **1**, 305-315 (1999)



Design of Equipment

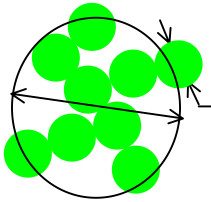
Predictions within 3% of product SSA (Gutsch, 1997)

H. Mühlenweg, A. Gutsch, A. Schild, C. Becker “Simulation for process and product optimization”, *Silica 2001, 2nd International Conference on Silica*, Mulhouse, France (2001) and
G. Vargas Commercializing Chemical Technology: Realization of Complete Solutions using Chemical Nanotechnology, Lecture at Nanofair, St. Gallen, Switzerland, Sept. 11, 2003.

Agglomerate and Primary Particle Size Definitions

Agglomerate Collision Diameter

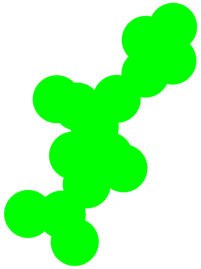
$$d_c = d_p \left(\frac{v}{v_p} \right)^{1/D_f}$$



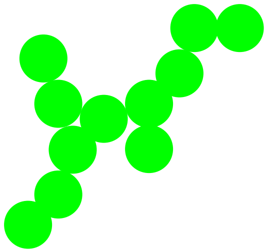
Primary Particle Diameter

$$d_p = \frac{6v}{\alpha}$$

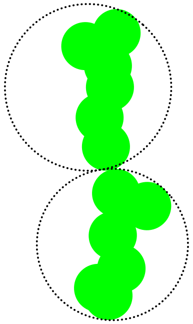
Hard Agglomerate



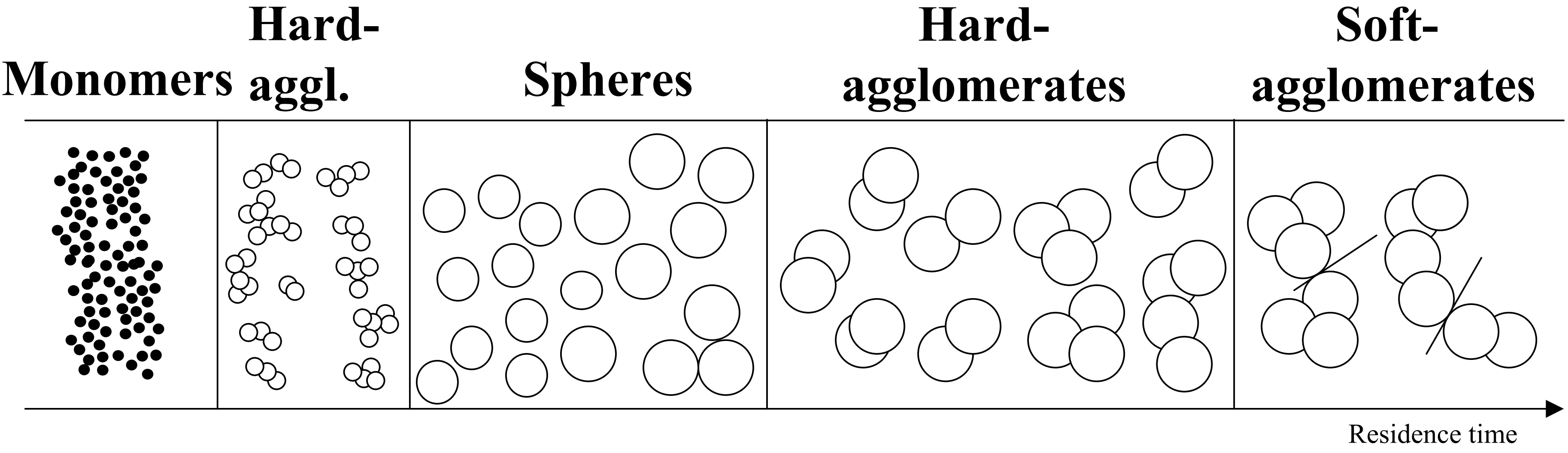
Soft Agglomerate
of Spherical Paticles



Soft Agglomerate

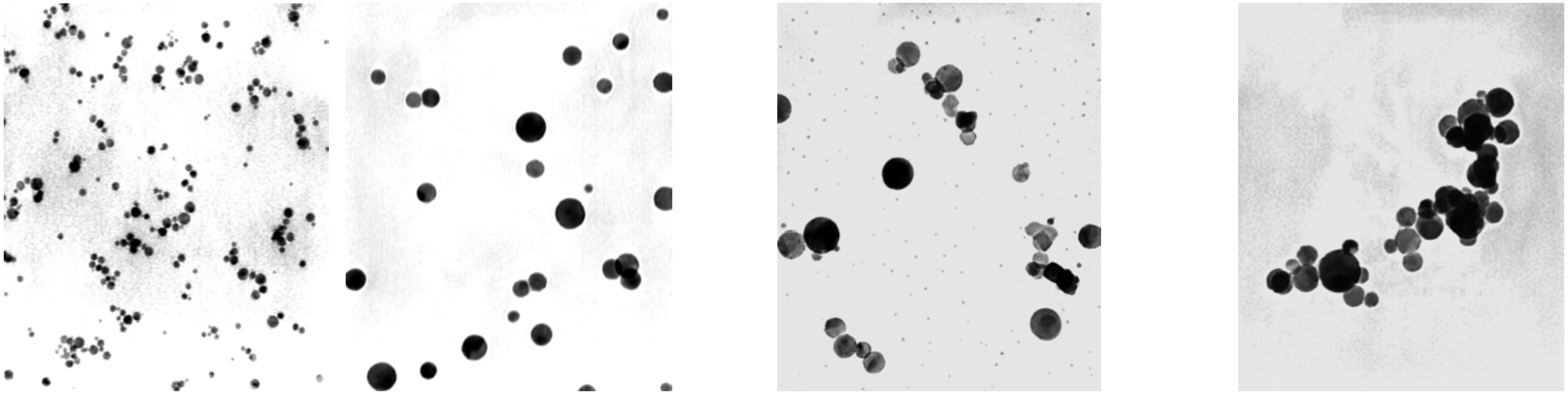


S. Tsantilis, S. E. Patsinis, "Soft- and Hard-agglomerate Aerosols made at High temperatures", *Langmuir*, in press (2004).

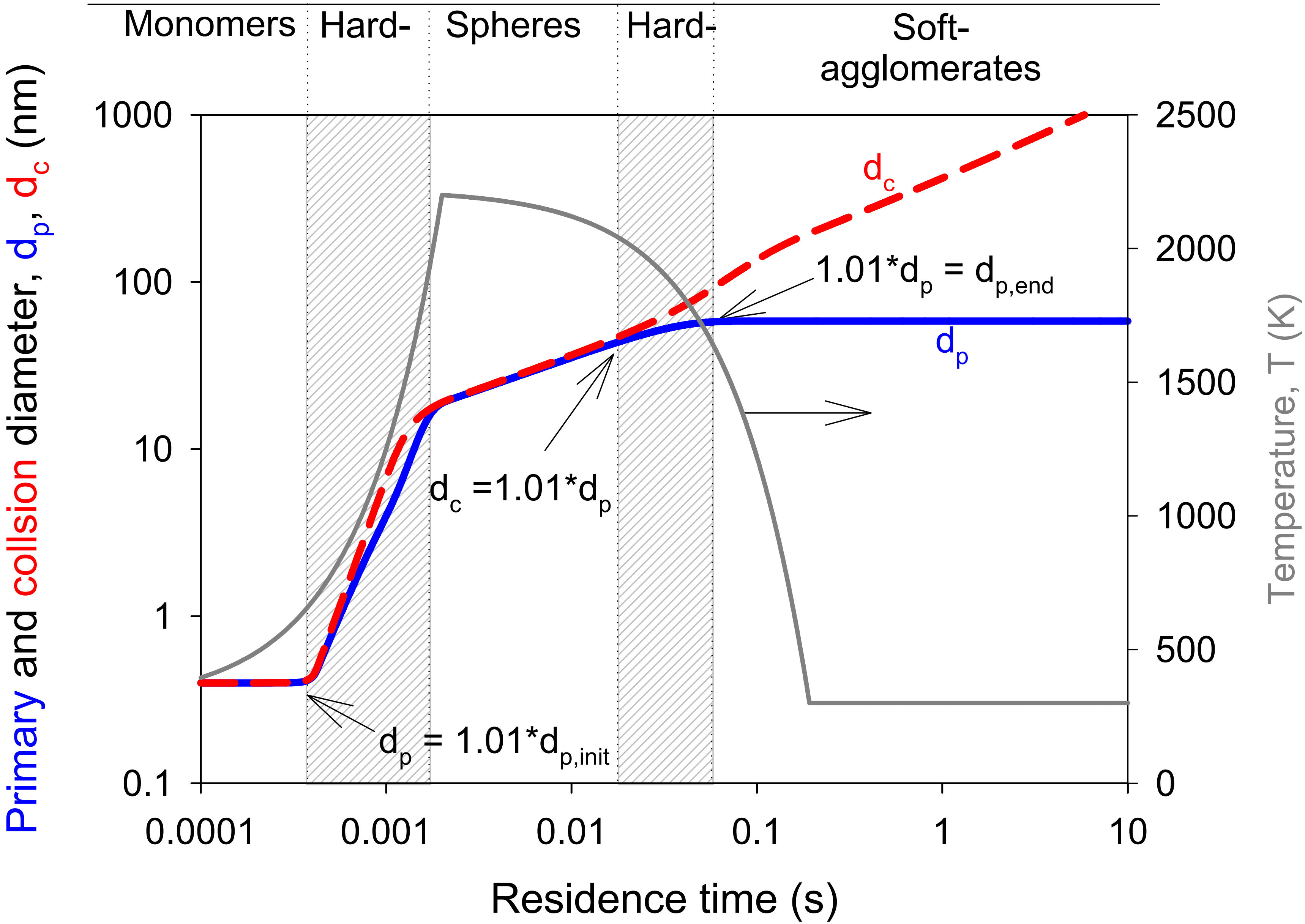


Monomers | **Hard-aggl.** | **Spheres** | **Hard-agglomerates** | **Soft-agglomerates**

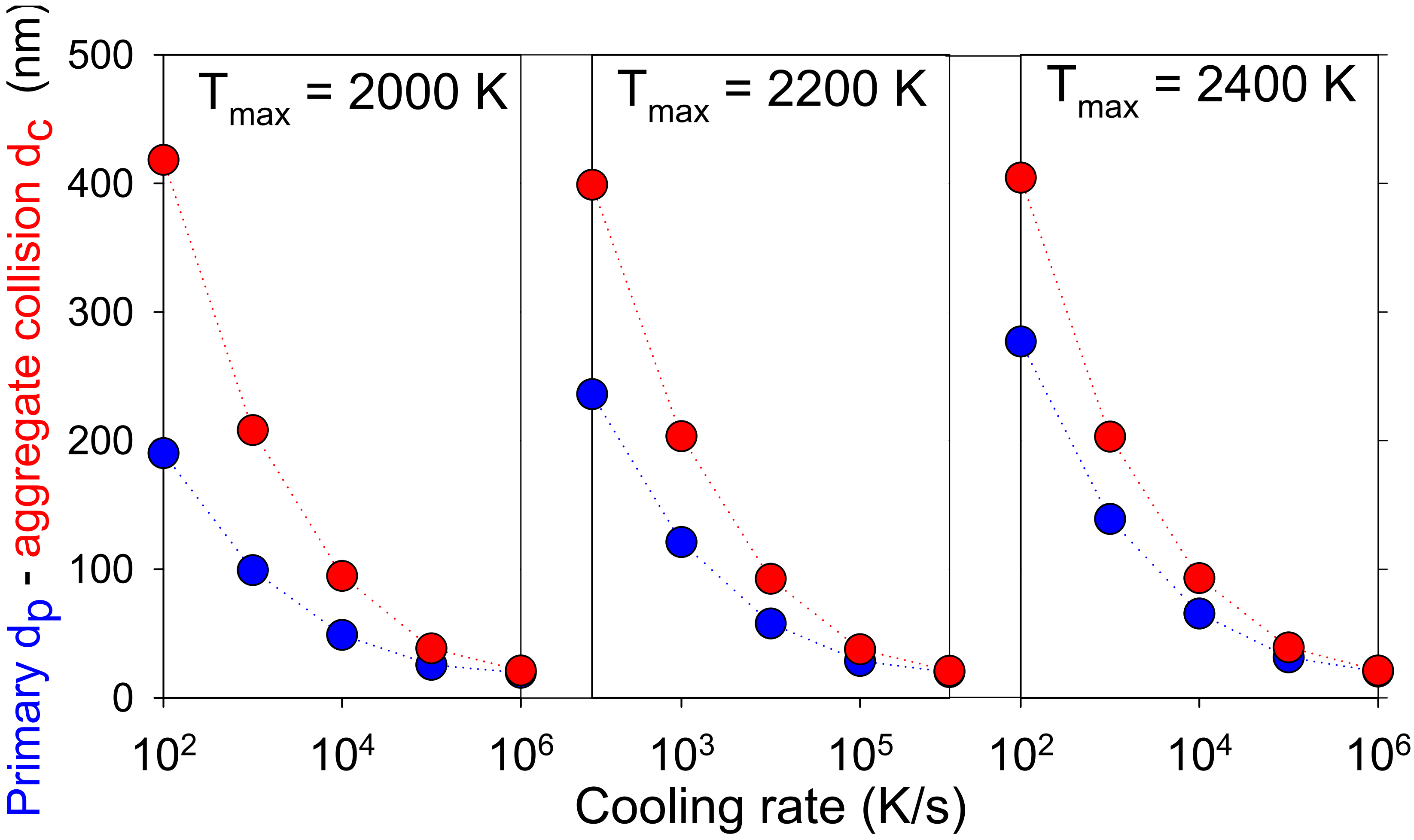
Residence time



Images from: Arabi-Katbi, O. I., Pratsinis, S. E., Morrison, P. W. and Megaridis, C. M. (2001), Monitoring the flame synthesis of TiO2 particles by in-situ FTIR spectroscopy and thermophoretic sampling. *Combust. Flame* **124**: 560-572.


Monomers
Hard-
Spheres
Hard-
Soft-agglomerates
Primary and collsion diameter, d_p, d_c (nm)
1000
100
10
1
0.1
Temperature, T (K)
2500
2000
1500
1000
500
0
0.0001
0.001
0.01
0.1
1
10
Residence time (s)
d_c
$1.01*d_p = d_{p,end}$
d_p
$d_c = 1.01*d_p$
$d_p = 1.01*d_{p,init}$

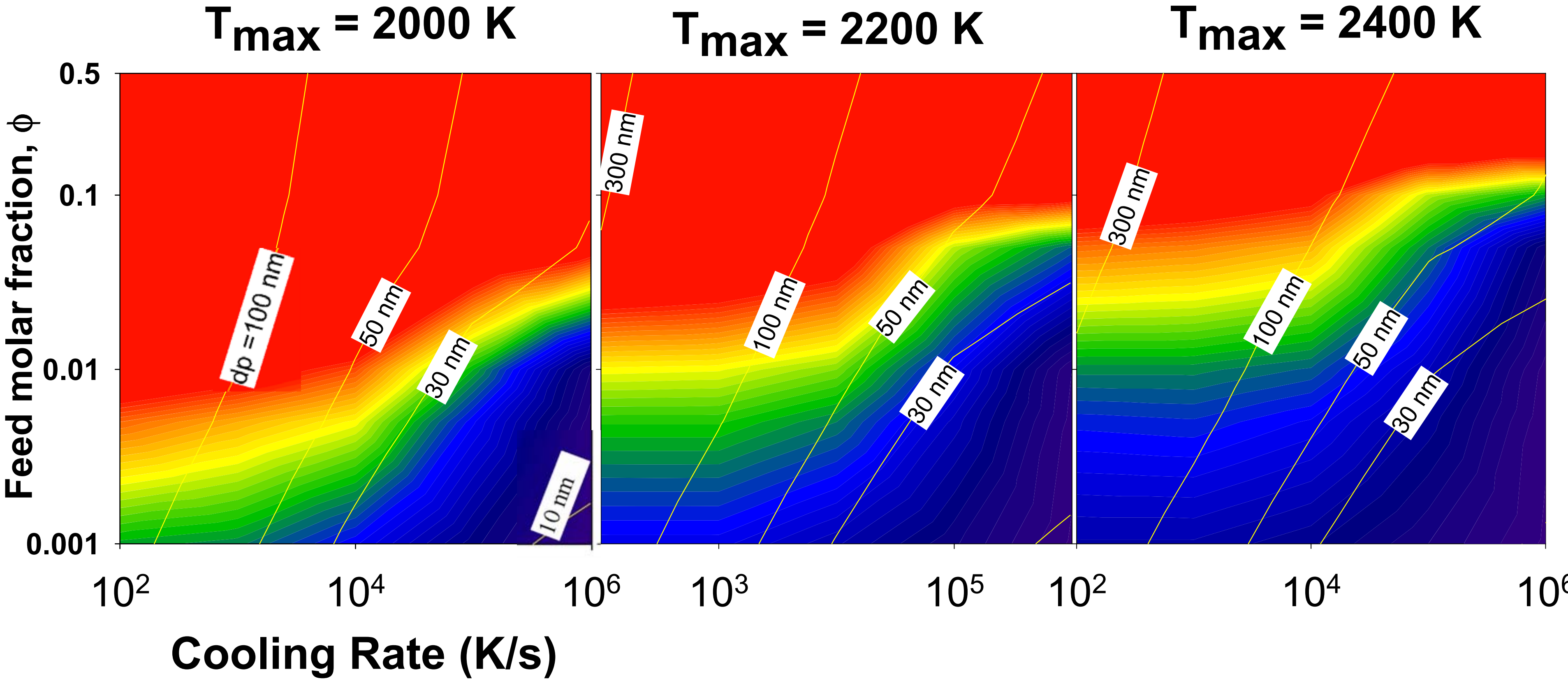
Effect of cooling rate on particle diameters



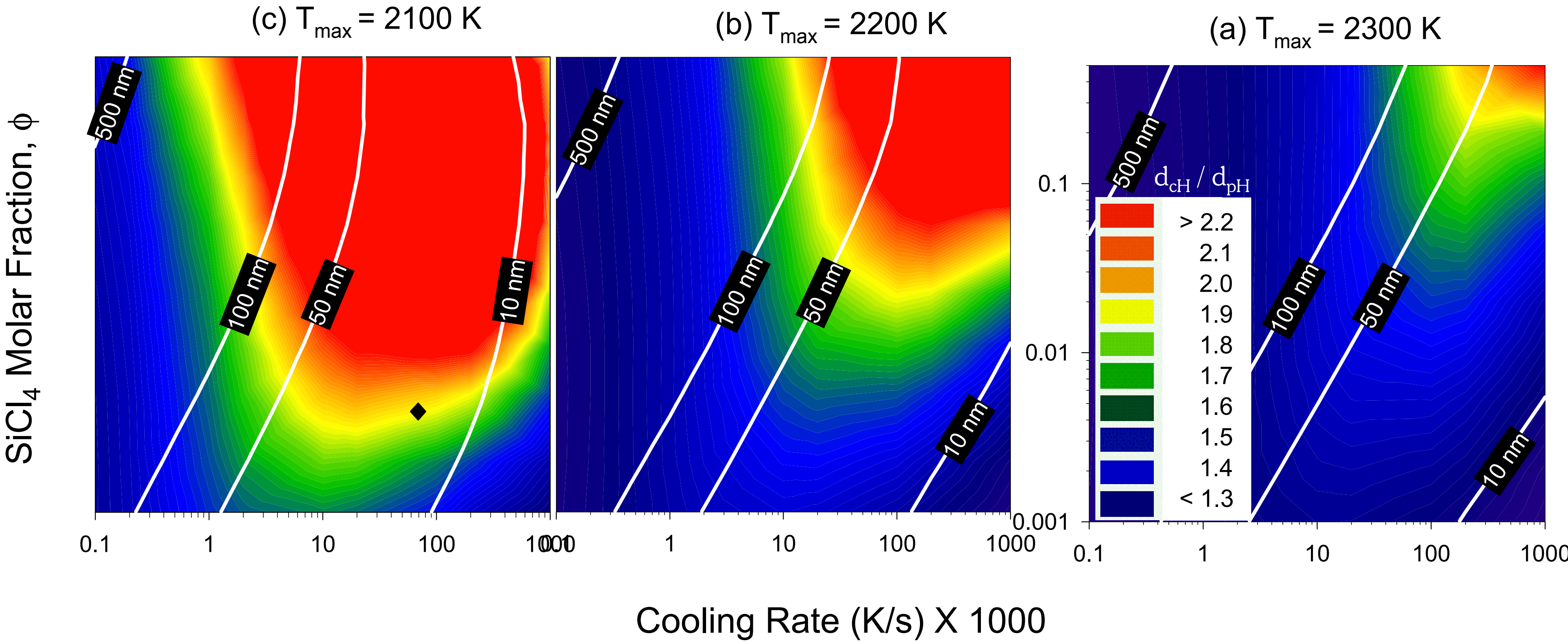
TiO_2: Maps for degree of agglomeration

d_c/d_p =

1	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2
🟪	🟪	🟦	🟦	🟦	🟩	🟩	🟨	🟧	🟧	🟥



SiO_2: Maps of Degree of Agglomeration ($h = d_{cH} / d_{pH}$)



S. Tsantilis, S. E. Patsinis, "Soft- and Hard-agglomerate Aerosols made at High temperatures", *Langmuir*, in press (2004).

Summary

- Regions of hard- and soft-agglomerates were identified in terms of maximum process temperature, T*max*, cooling rate, CR, and precursor initial concentration, C_0.

- Increasing cooling rate decreased the hard-agglomerate collision and primary particle diameters.

- Lightly agglomerated SiO_2 particles are formed at high T*max* and high CR nearly regardless of C_0

- In contrast, for TiO_2, the C_0 determines the agglomeration state and to a lesser extent T*max* while CR hardly affects it.

- Predictions were consinstent with experimental data.

Gas-Phase (Aerosol) Synthesis of Nanoparticles: Scale-up

Karsten Wegner and Sotiris E. Pratsinis
Particle Technology Laboratory
Department of Mechanical and Process Engineering
ETH Zurich
CH-8092 Zurich, Switzerland

Supported by the
Swiss Commission for Technology and Innovation

Overview of Scale-up

Vapor-fed Diffusion Flames

Burner Geometry & Reactant Mixing

Reactor Operation Lines and Correlations

Liquid-fed Spray Flames

Metal/Ceramic & Hollow Particles

Conclusions

Flames for manufacture of inorganic nanoparticles

Established advantages

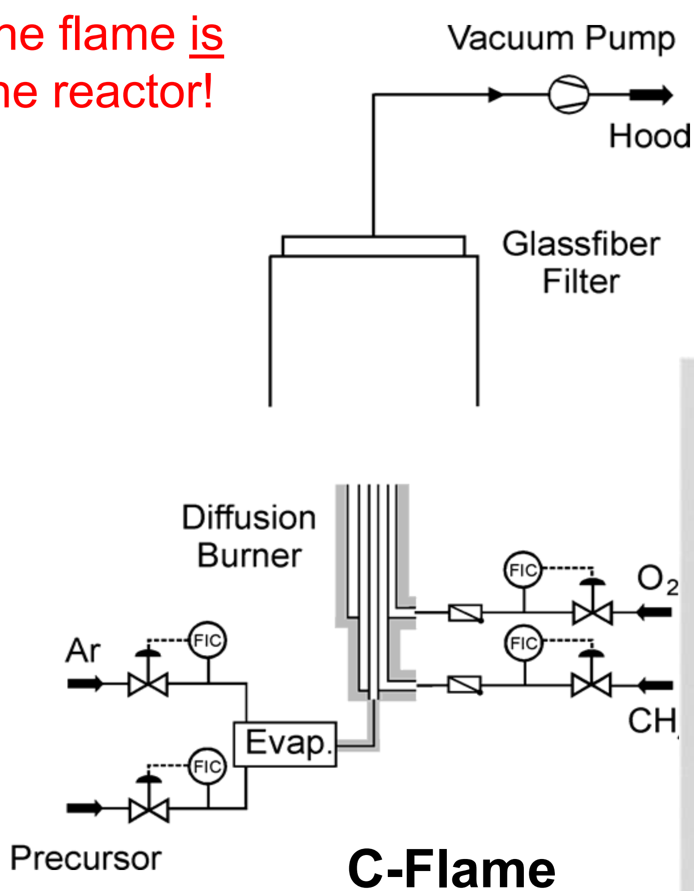
- High purity product
- Easy collection
- No liquid waste
- Scalable process
- No moving parts

Research challenges

- Agglomerates
- Limited size control
- Multicomponent
  - ceramic/ceramic
  - metal/ceramic

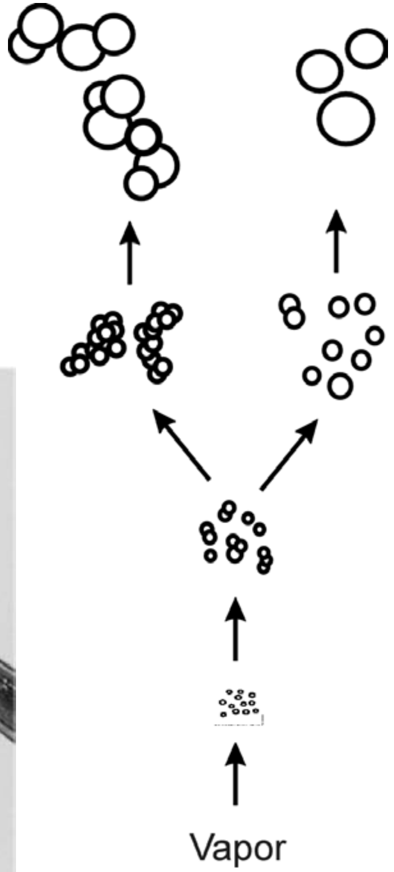
Diffusion Flames:
Flexible, Simple and Safe Technology

The flame is the reactor!



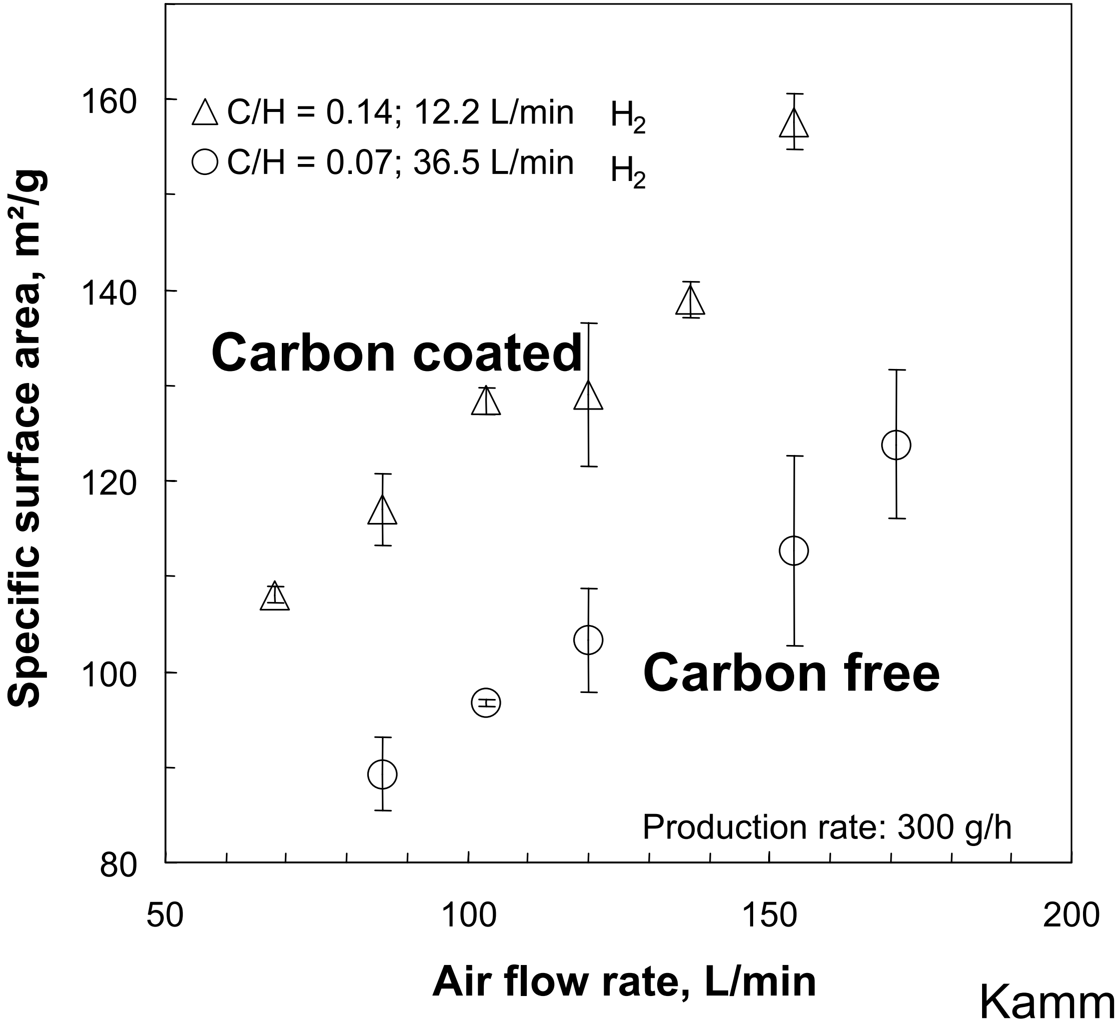
C-Flame

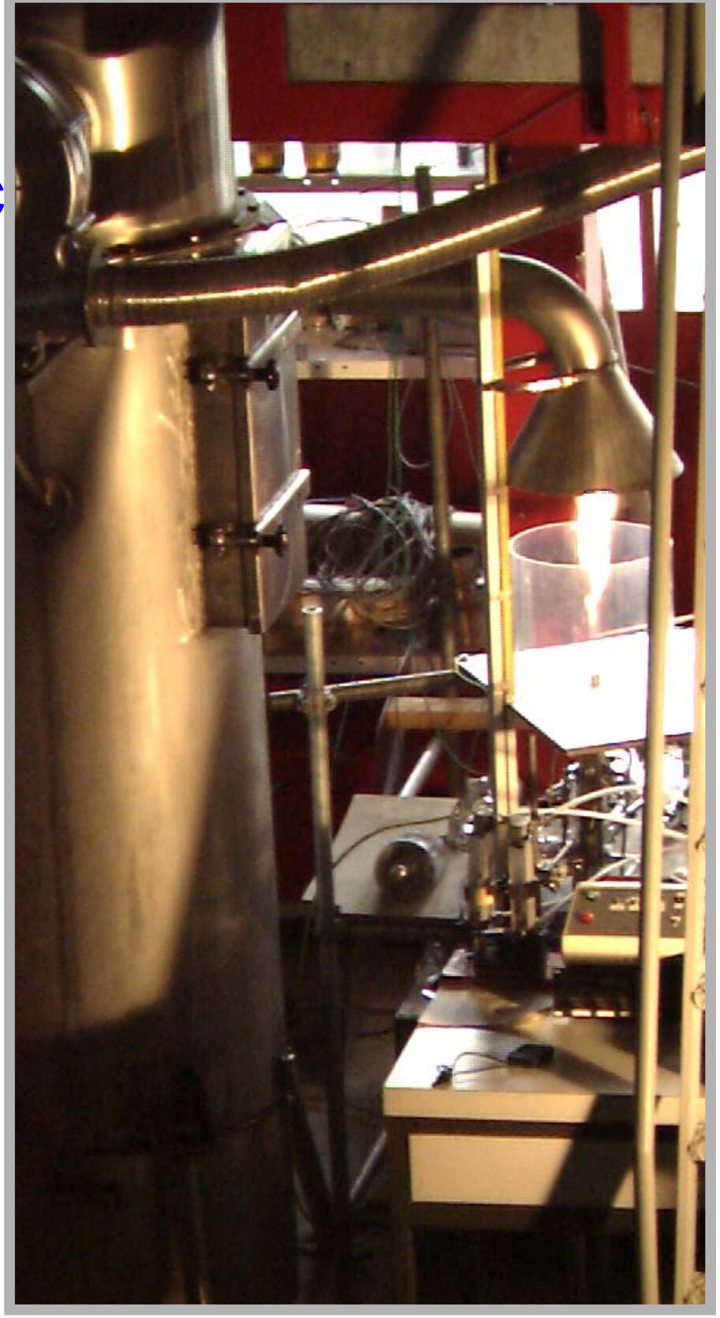
Flame Temperature,
Cooling Rate,
Particle Concentration,
Residence Time



Particle Growth

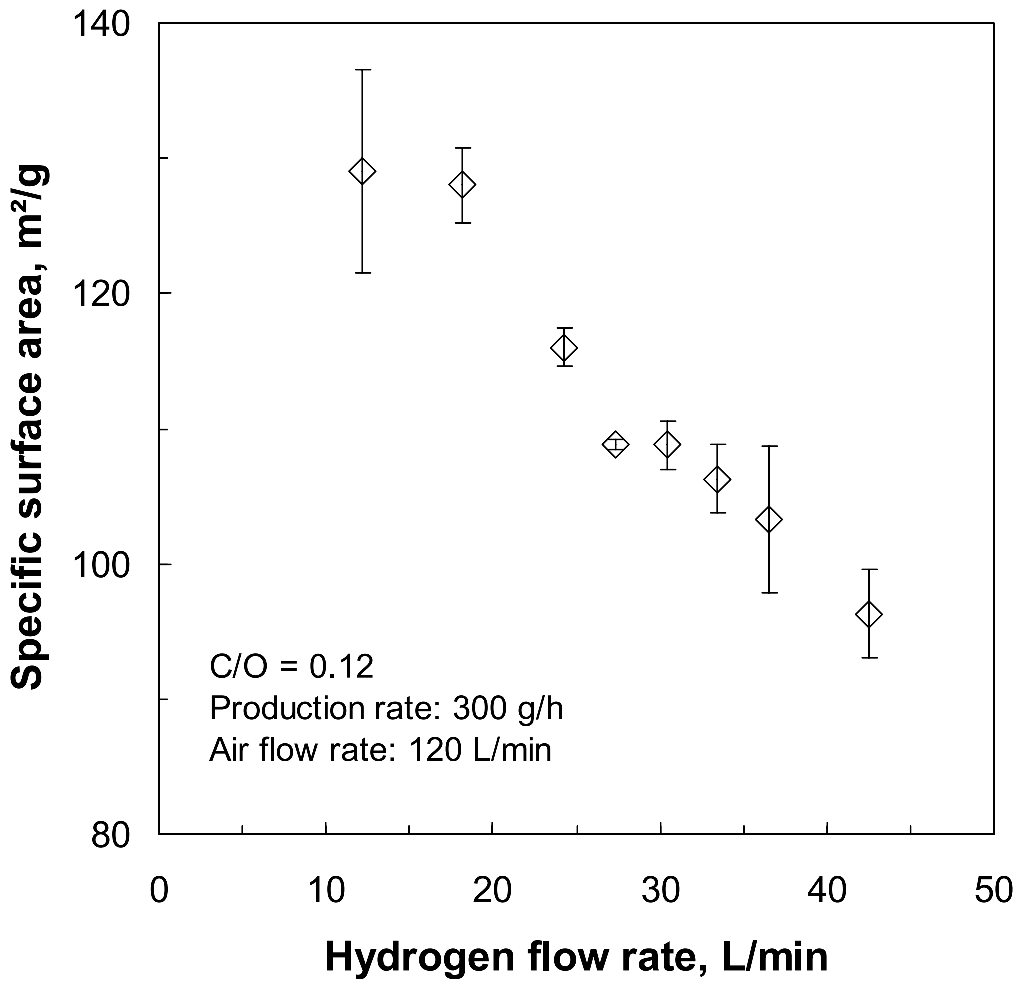
Carbon-coated silica: Effect of air flow rate on product specific surface area made at 300 g/h





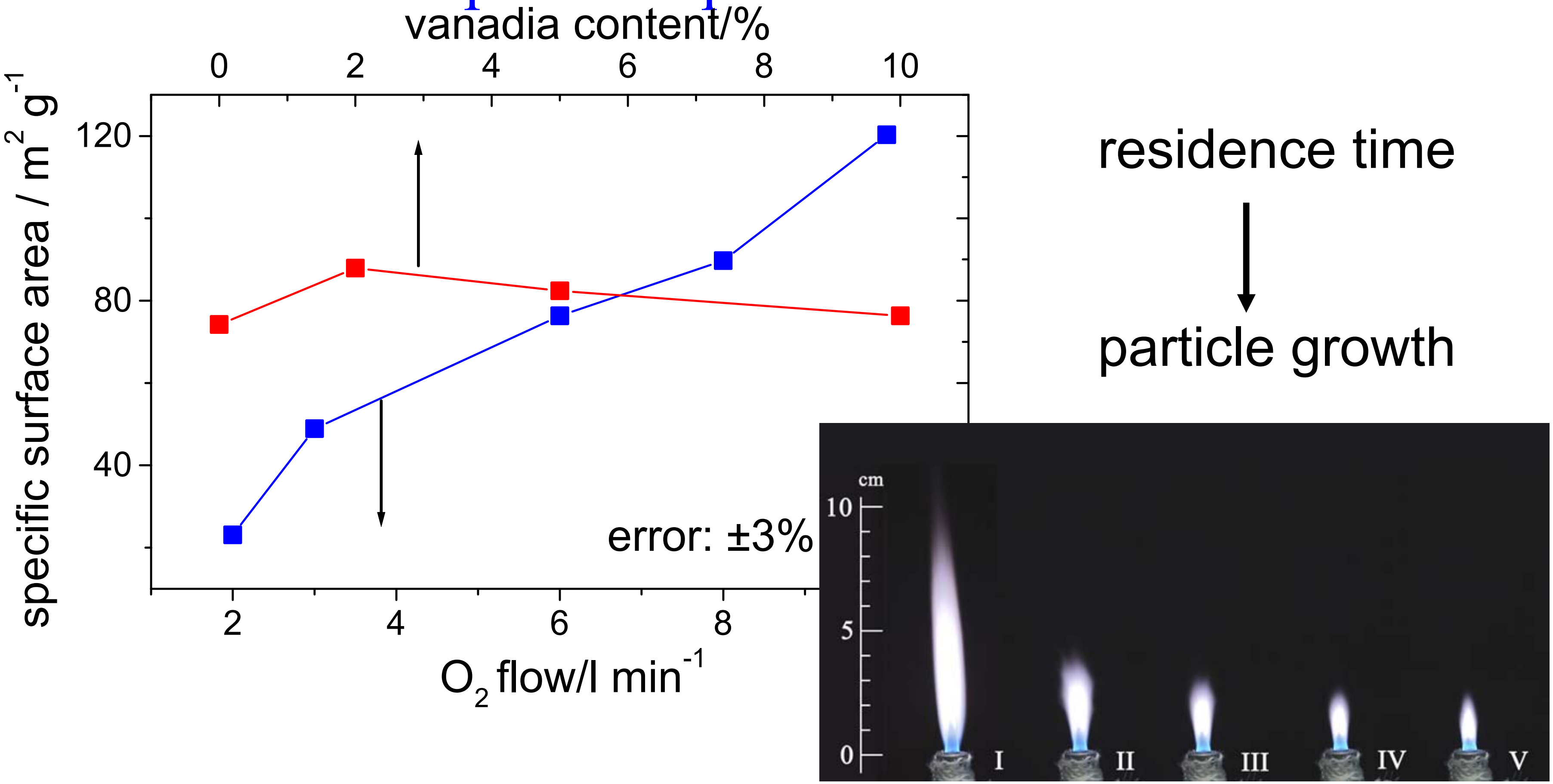
Kammler et al. *AIChE J*. **47**, 1533 (2001)

Carbon-coated-silica: Effect of hydrogen (fuel) flow rate on product specific surface area made at 300 g/h



Kammler et al. *AIChE J*. **47**, 1533 (2001)

Vanadia-coated titania catalysts: Effect of oxidant flow rate on product specific surface area



residence time

↓

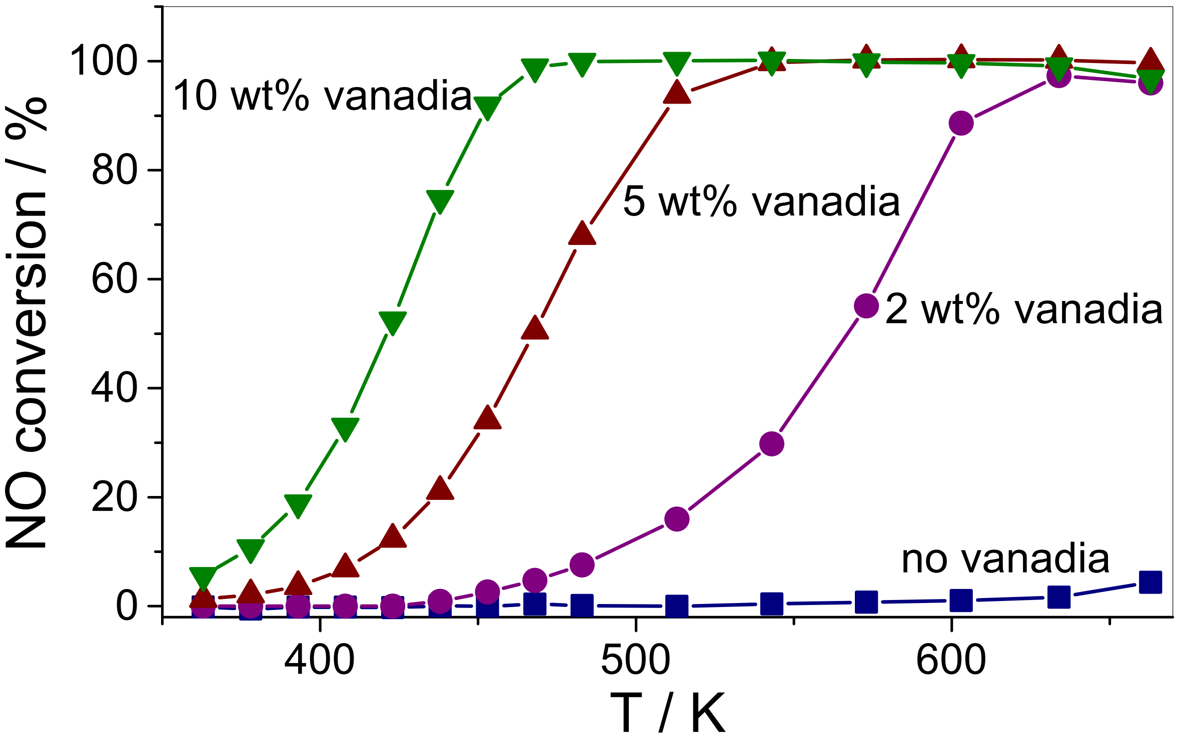
particle growth

Flames with 2, 3, 6, 8, 10 l O_2/min

Stark, Wegner, Pratsinis, Baiker, *J. Catal.* **197**, 182 (2001)

V_2O_5-TiO_2: Selective catalytic reduction (SCR) with NH_3 as a function of V content

$$NO + NH_3 \xrightarrow{O_2} N_2 + H_2O$$

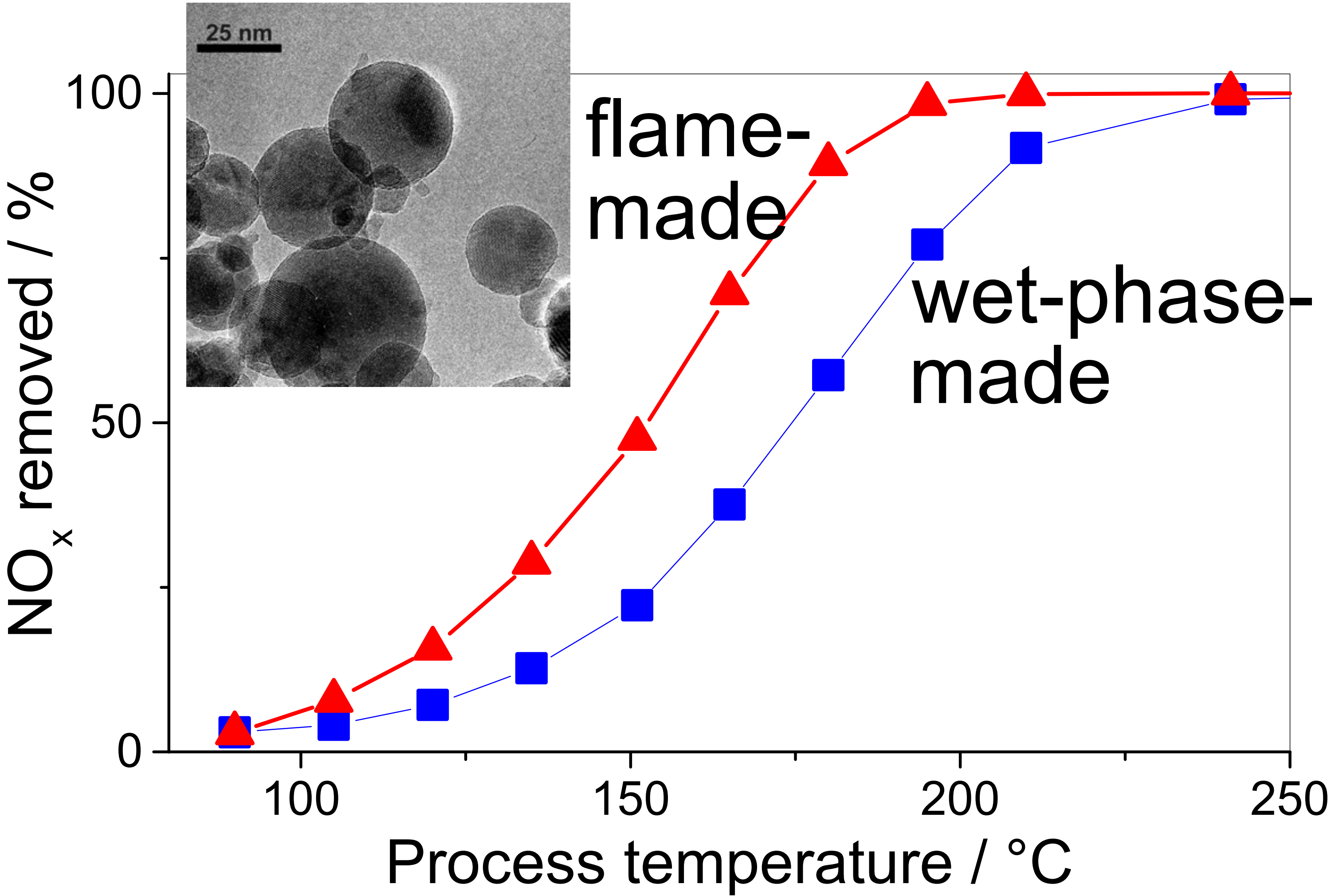


Conditions:

- 900 ppm NO
- 900 ppm NH_3
- 1.8 vol% O_2 in He
- space velocity: 24’000 h^{-1}
- all ca. 50 m^2/g

Stark, Wegner, Pratsinis, Baiker, *J. Catal.* **197**, 182 (2001)

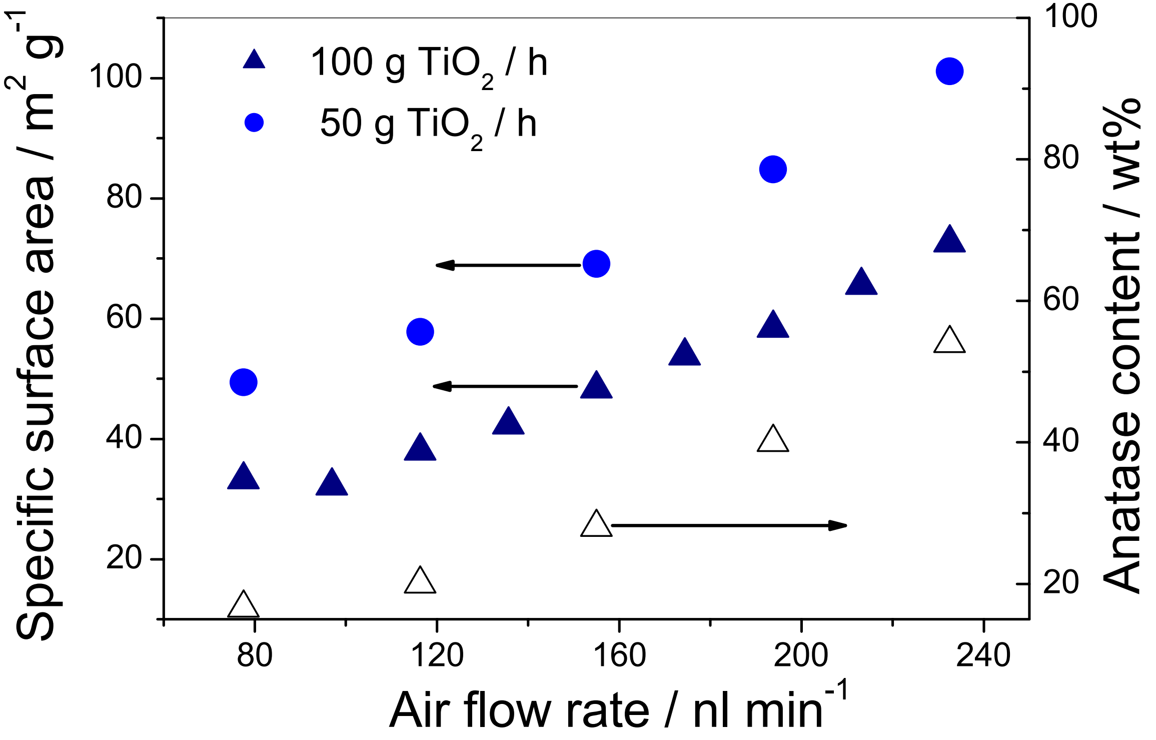
Comparison of flame-made with conventional wet-made catalysts



Stark, Wegner, Pratsinis, Baiker, *J. Catal.* **197**, 182 (2001)

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Scale-up of V_2O_5-TiO_2 production in a H_2/air flame

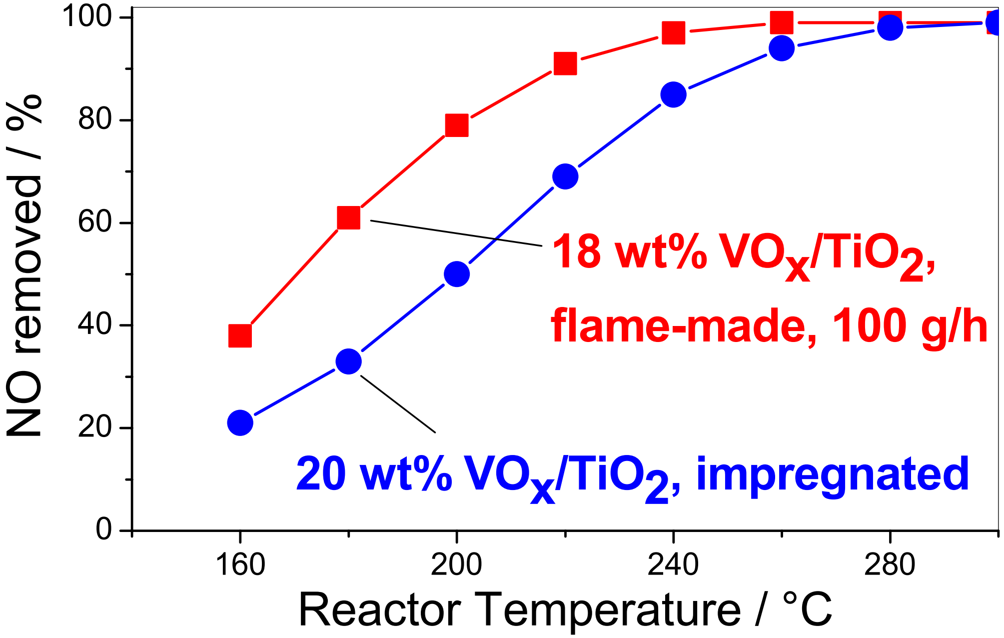


H_2/air flame;
1.8 m^3 H_2/h:

phase composition:
Rutile & Anatase

•W. J. Stark, A. Baiker, S. E. Pratsinis, *Part. Part. Sys. Charact.*, **19**, 306-311 (2002)

V_2O_5-TiO_2 catalysts: Comparison to conventional DeNOx catalysts @ U. Essen (Prof. Cramer)



Fixed bed pilot-scale test reactor, 2.4 cm/sec

Gas composition:
-400 ppm NO
-400 ppm NH_3
-10 vol% oxygen in nitrogen

Reference:
-impregnated Degussa P 25
-same V content in both catalysts
-specific surface area: 50-55 m^2/g

- W. J. Stark, A. Baiker, S. E. Pratsinis, *Part. Part. Sys. Charact*. **19**, 306-311 (2002)

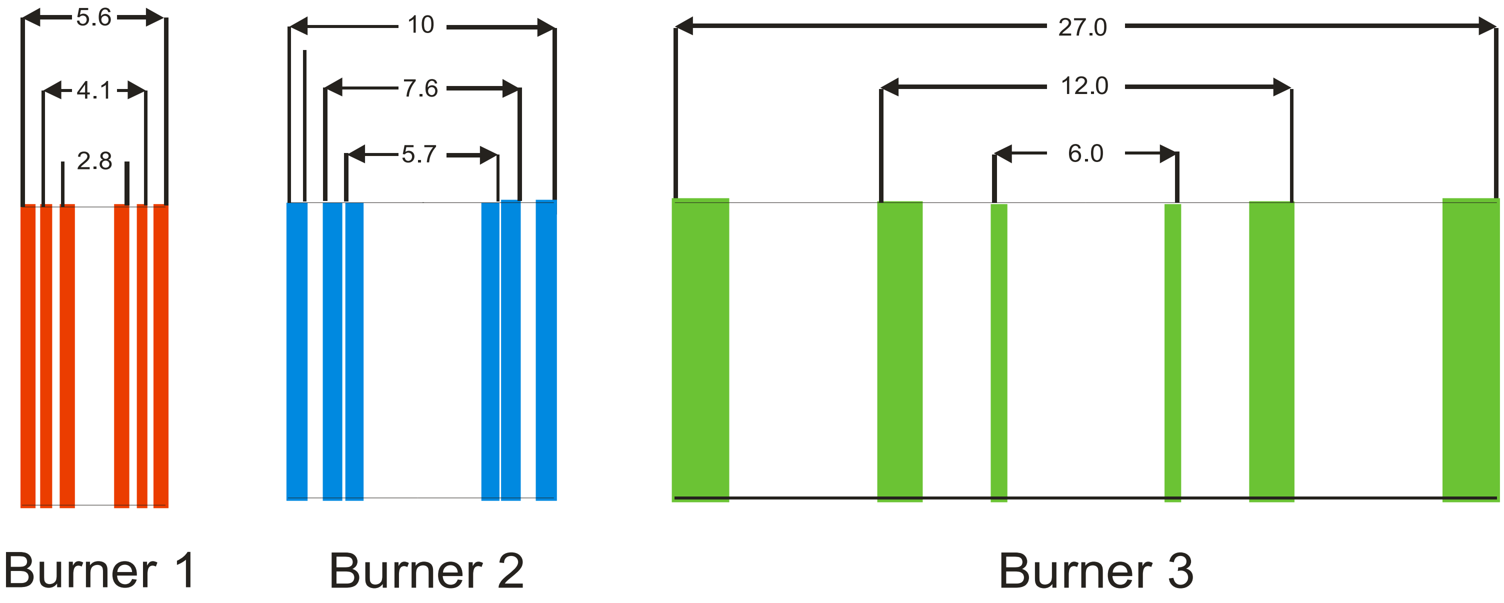
Reactant flow rates for control of flame-made particle characteristics

- Zhu et al. 1996,1997 (SiO_2, SnO_2)
- Briesen et al., 1998 (SiO_2)
- Johannessen et al., 2000 (Al_2O_3)
- Cho and Choi, 2000 (SiO_2)
- Jang and Kim, 2001 (TiO_2)

However, reactant flow rates are inadequate to compare different burners or to derive design correlations for flame aerosol reactor scale-up.

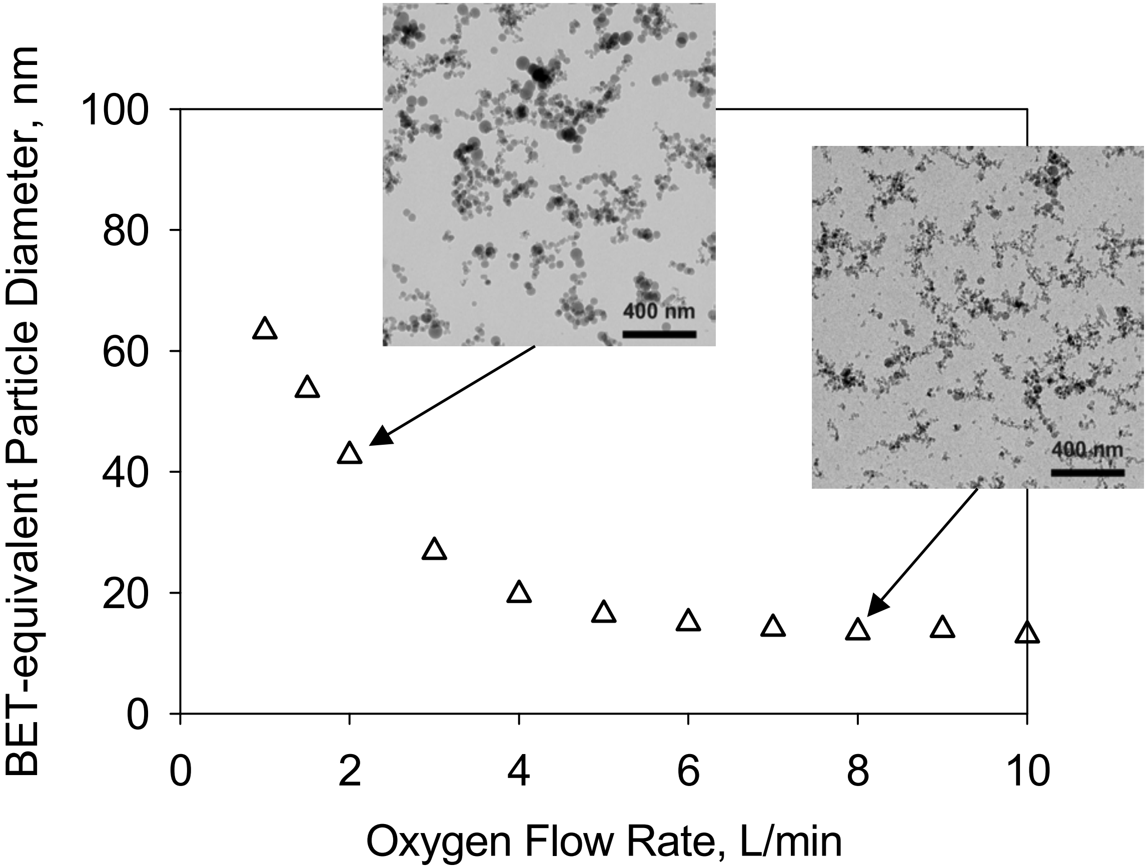
Variation of Burner Geometry

Wegner, Pratsinis, "Scale-up of nanoparticle synthesis in diffusion flame reactors," *Chem. Eng. Sci.* **58**, 4581-4589 (2003).

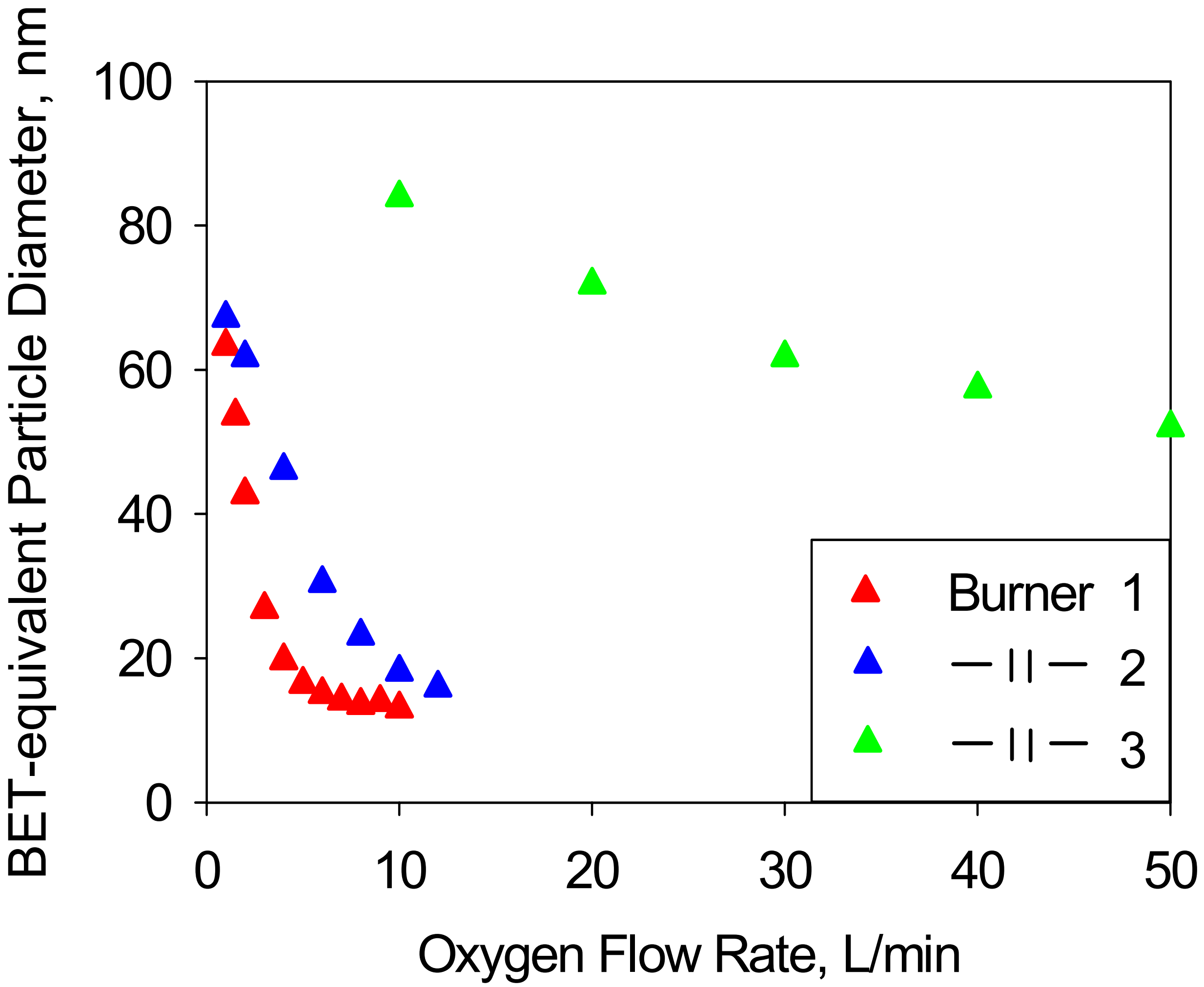


Dimensions in mm

Burner 1: Control of Silica Primary Particle Diameter by the O_2 Flow Rate



Separate Operation Lines for each Burner



Conditions:

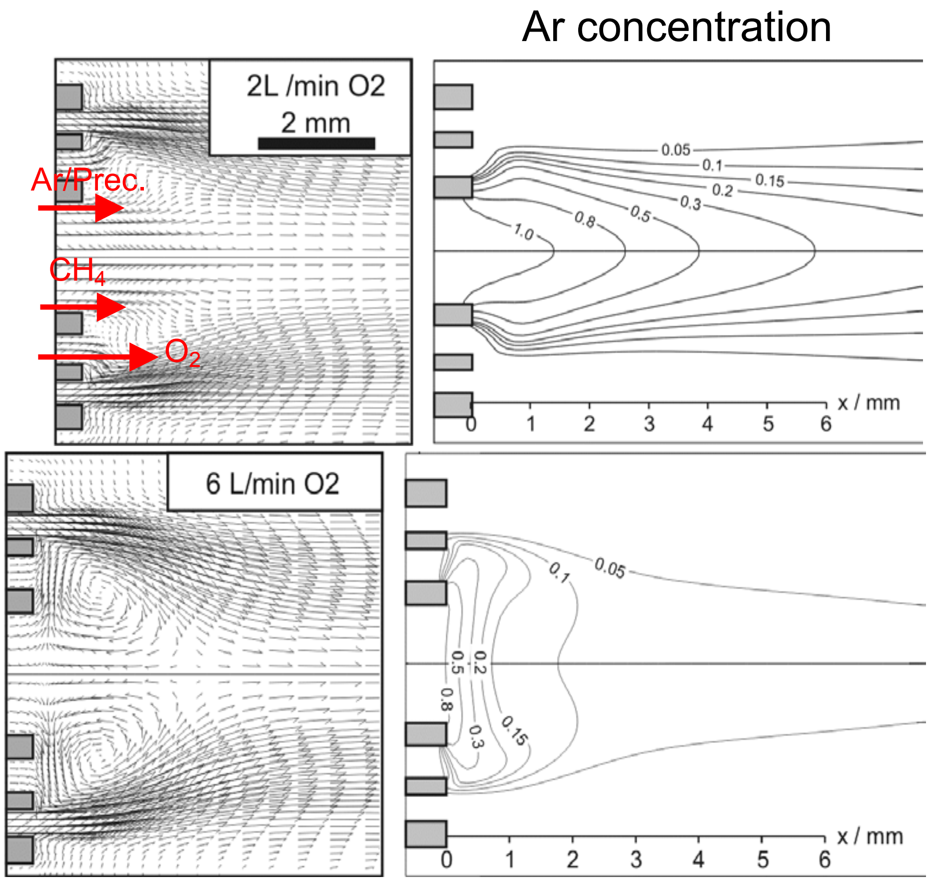
CH_4: 0.5 L/min

Ar: 0.3 L/min

SiO_2: 5 g/h

Diffusion Flames: Coaxial Jet Mixing

Cold flow CFD profiles:



Diffusion Flames:

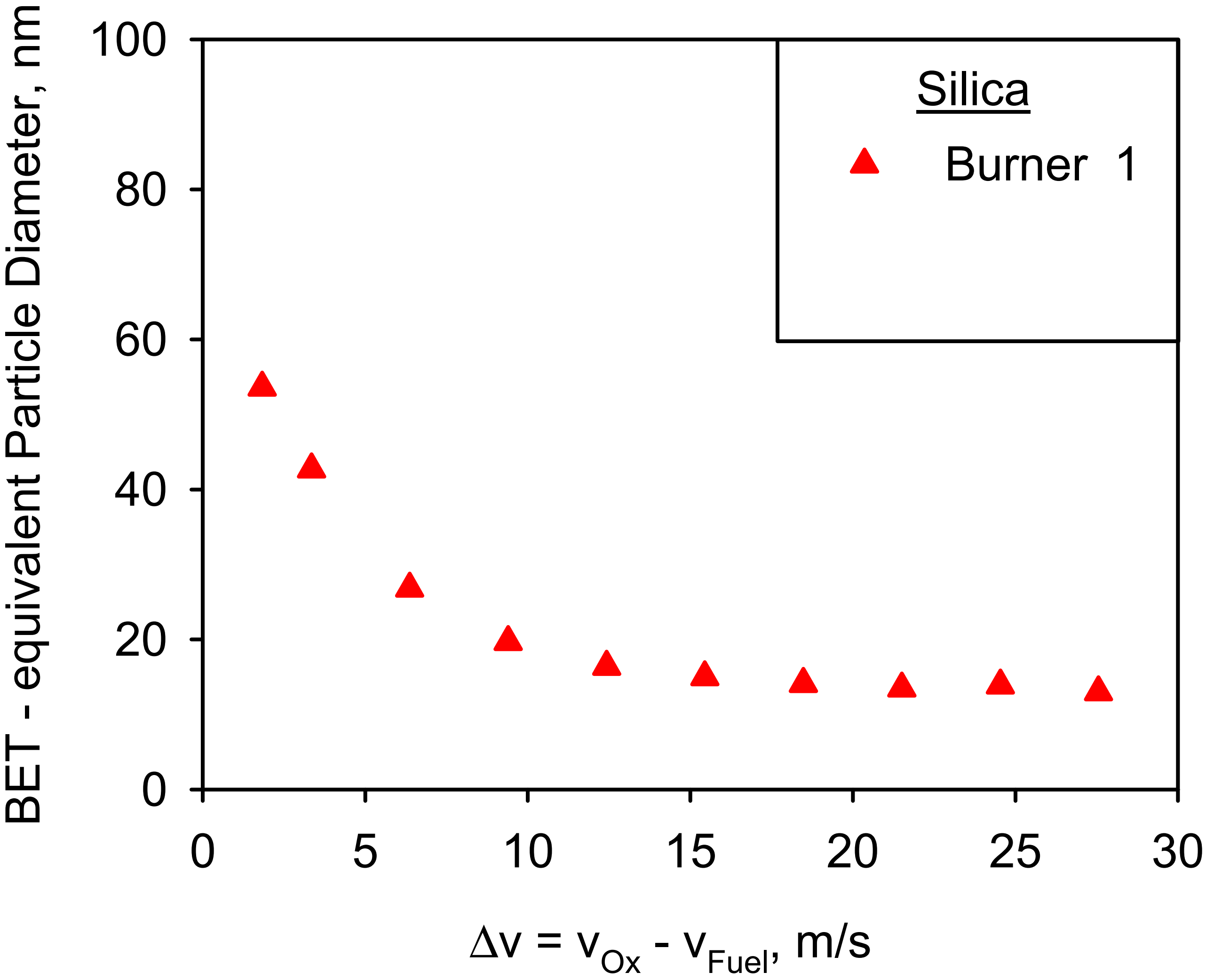
$$t_{reaction} << t_{mixing}$$

Particle Formation takes place upon mixing of precursor and oxidant.

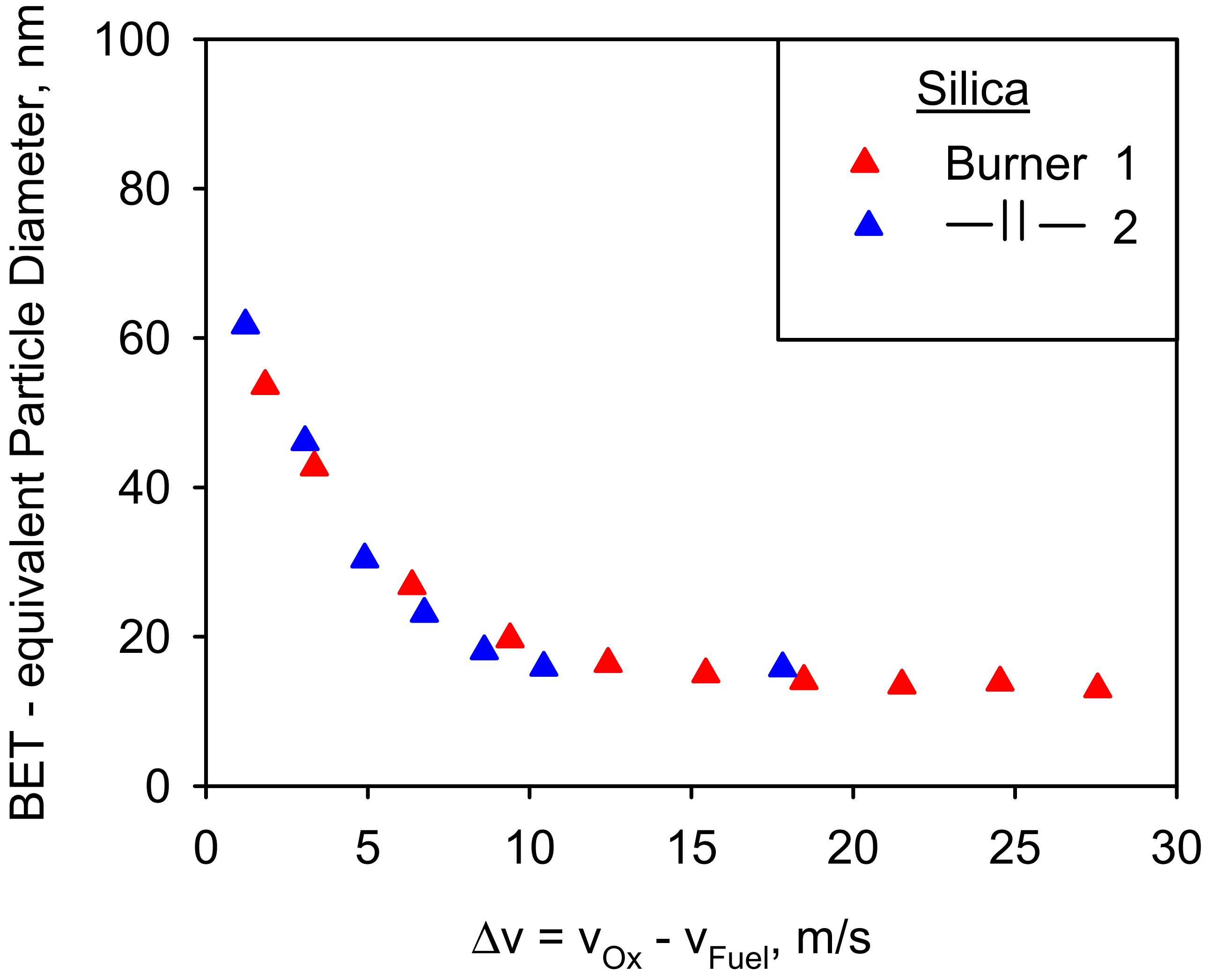
Similar reactant mixing for similar velocity difference $\Delta v = v_{Ox} - v_{Fuel}$

$$\underbrace{v_{Ar+Prec.} \approx v_{CH_4}}_{v_{Fuel}} \leq v_{Ox}$$

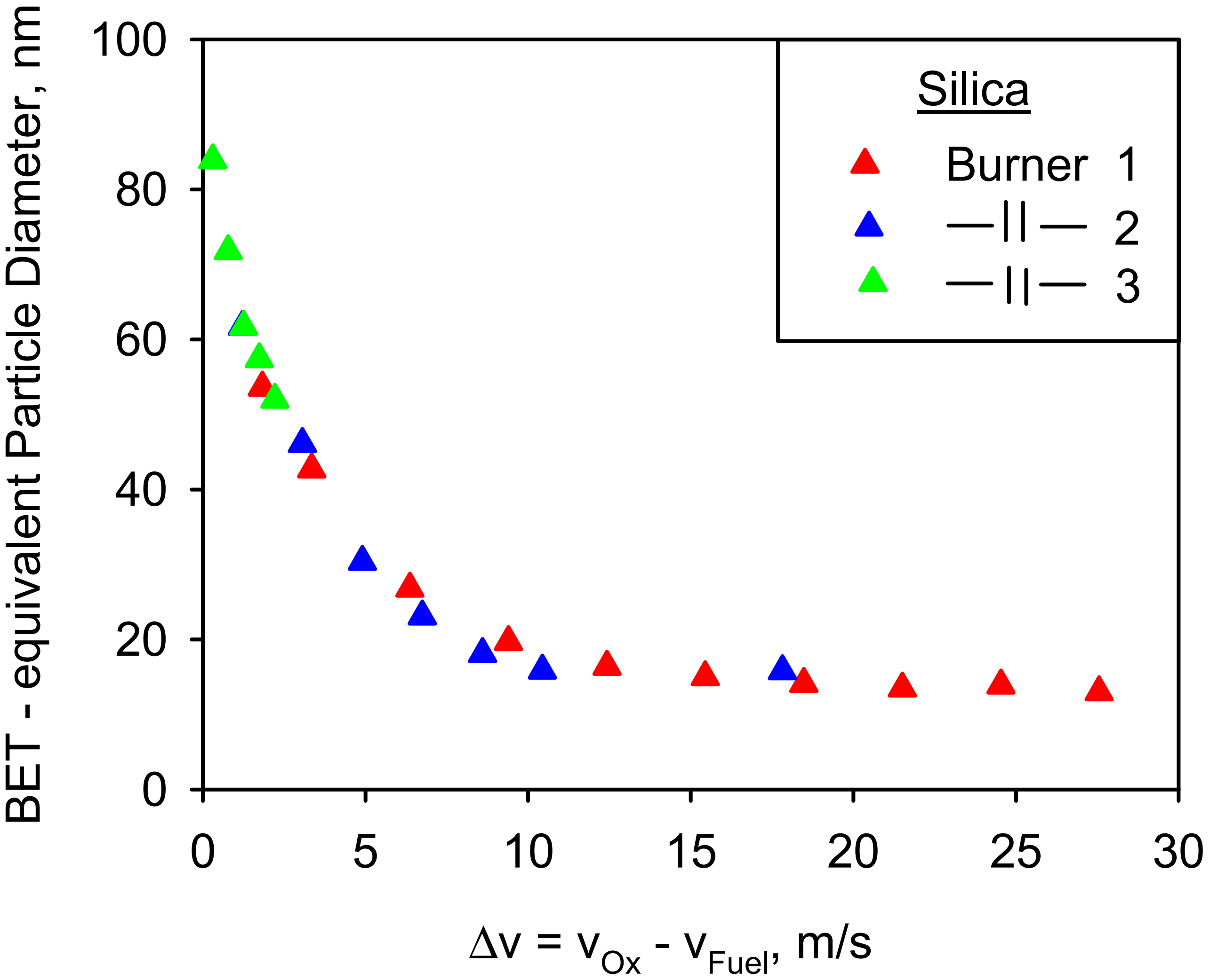
Single Operation Line $d_p = f(\Delta v)$



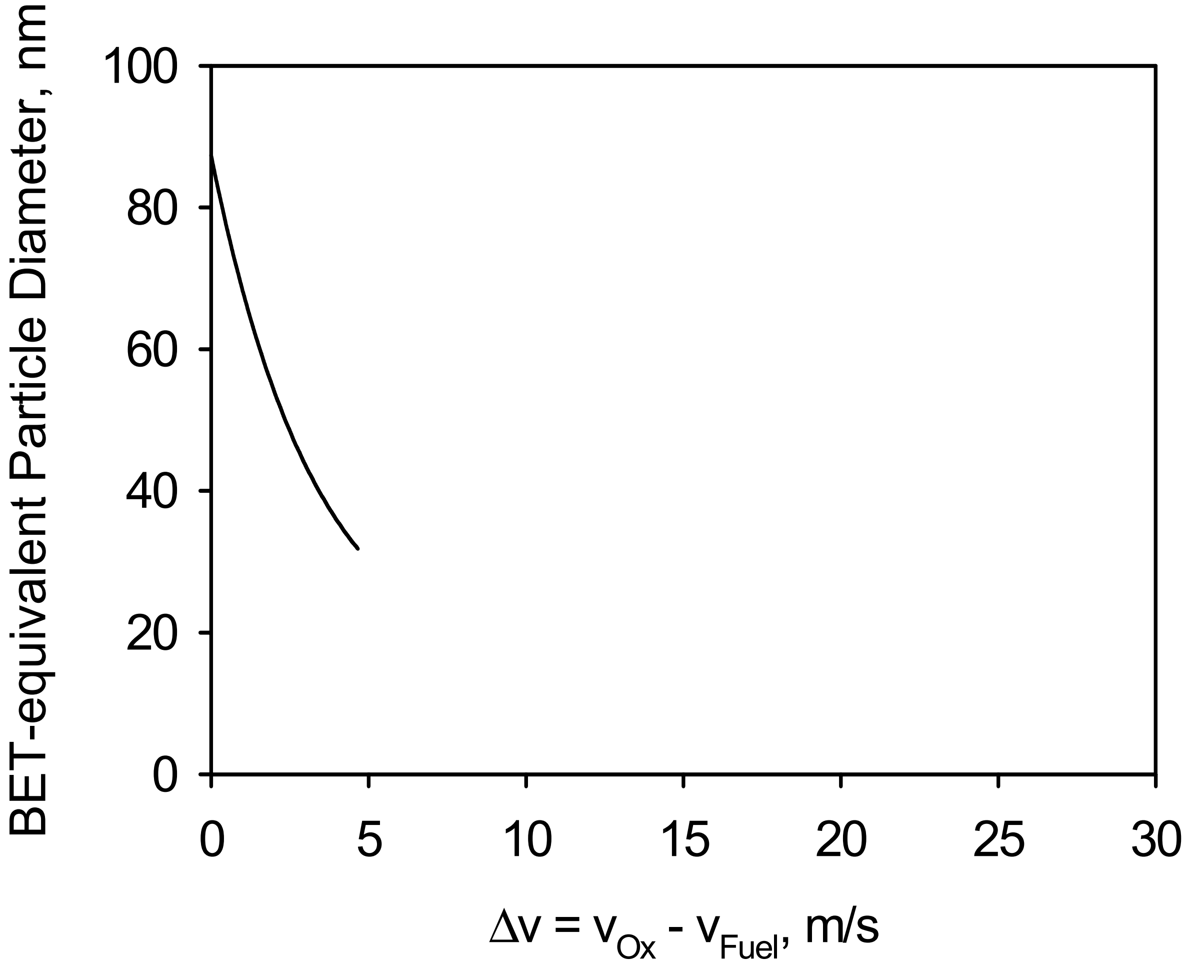
Single Operation Line $d_p = f(\Delta v)$



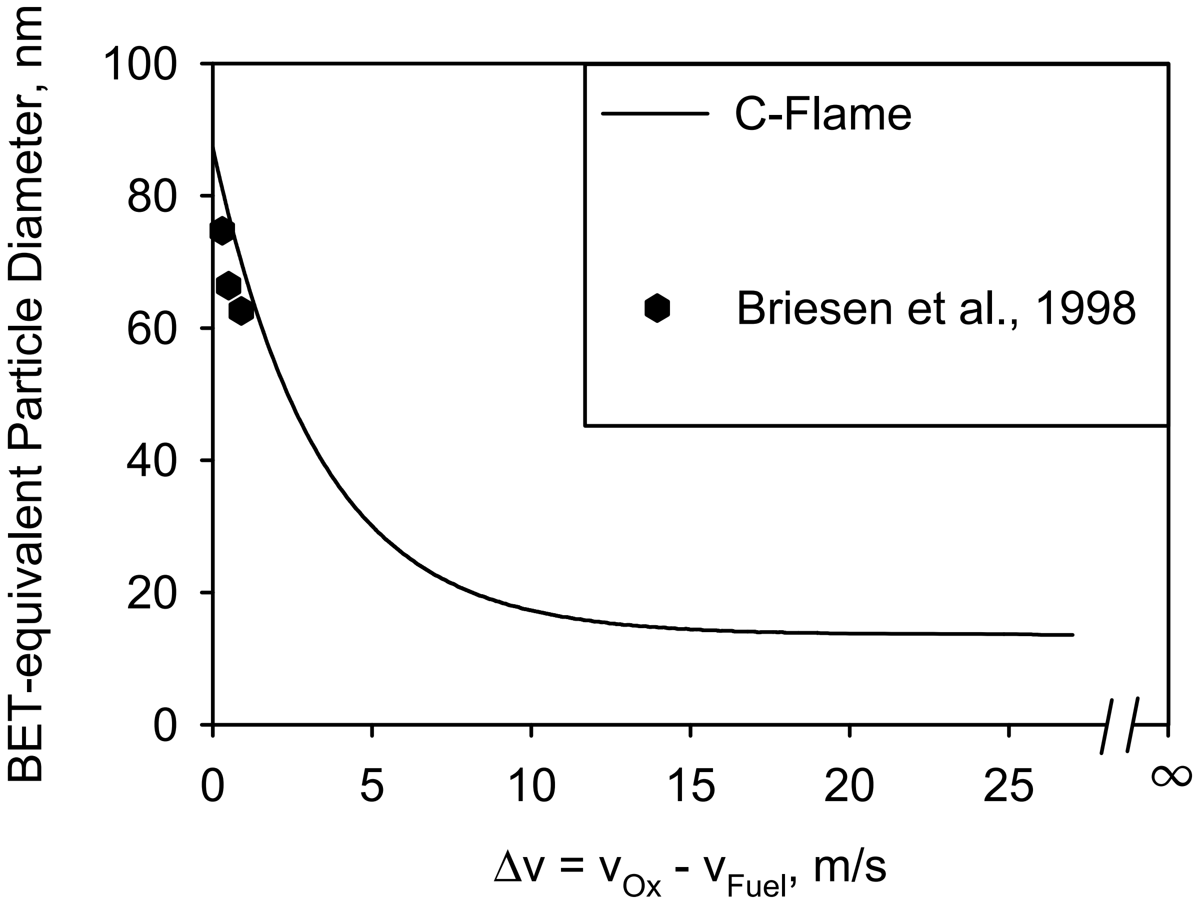
Single Operation Line $d_p = f(\Delta v)$



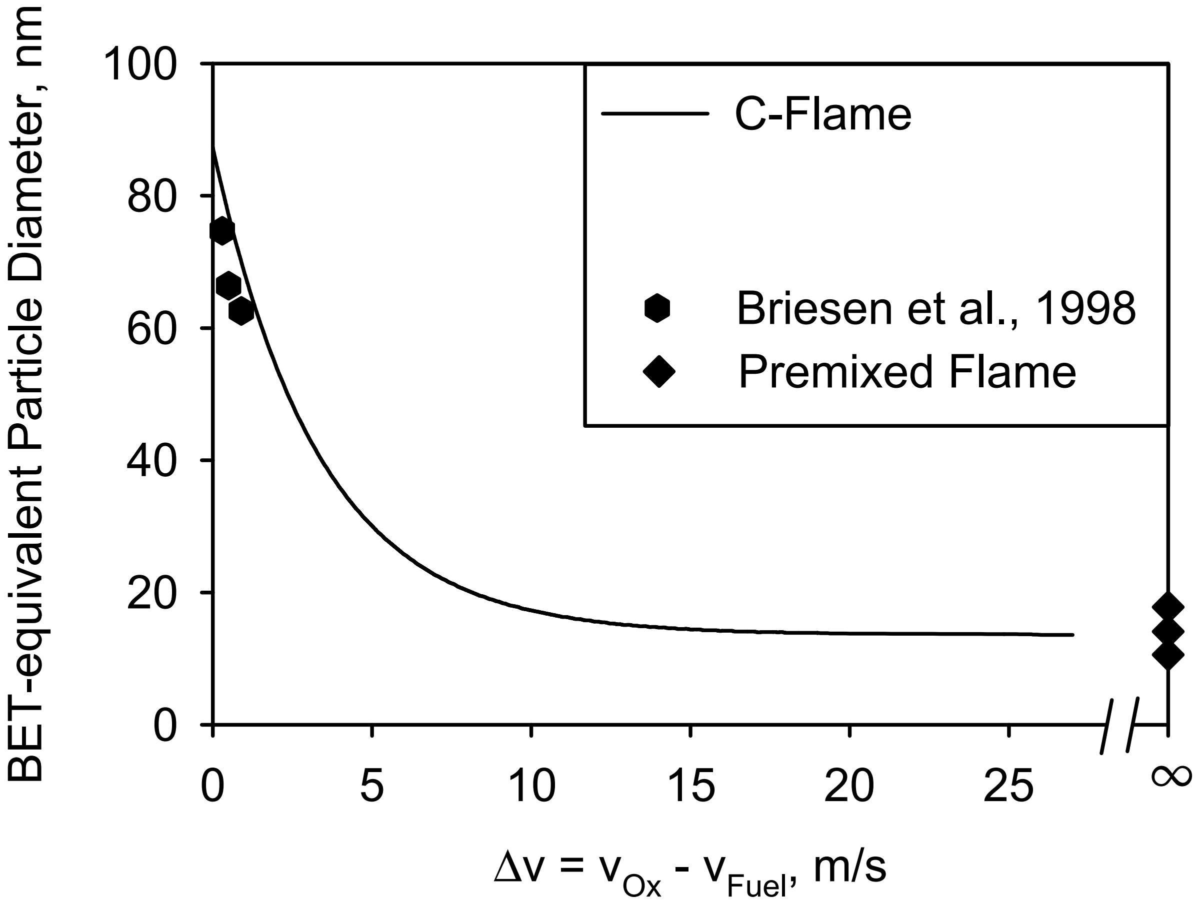
Operation Line for Silica synthesis



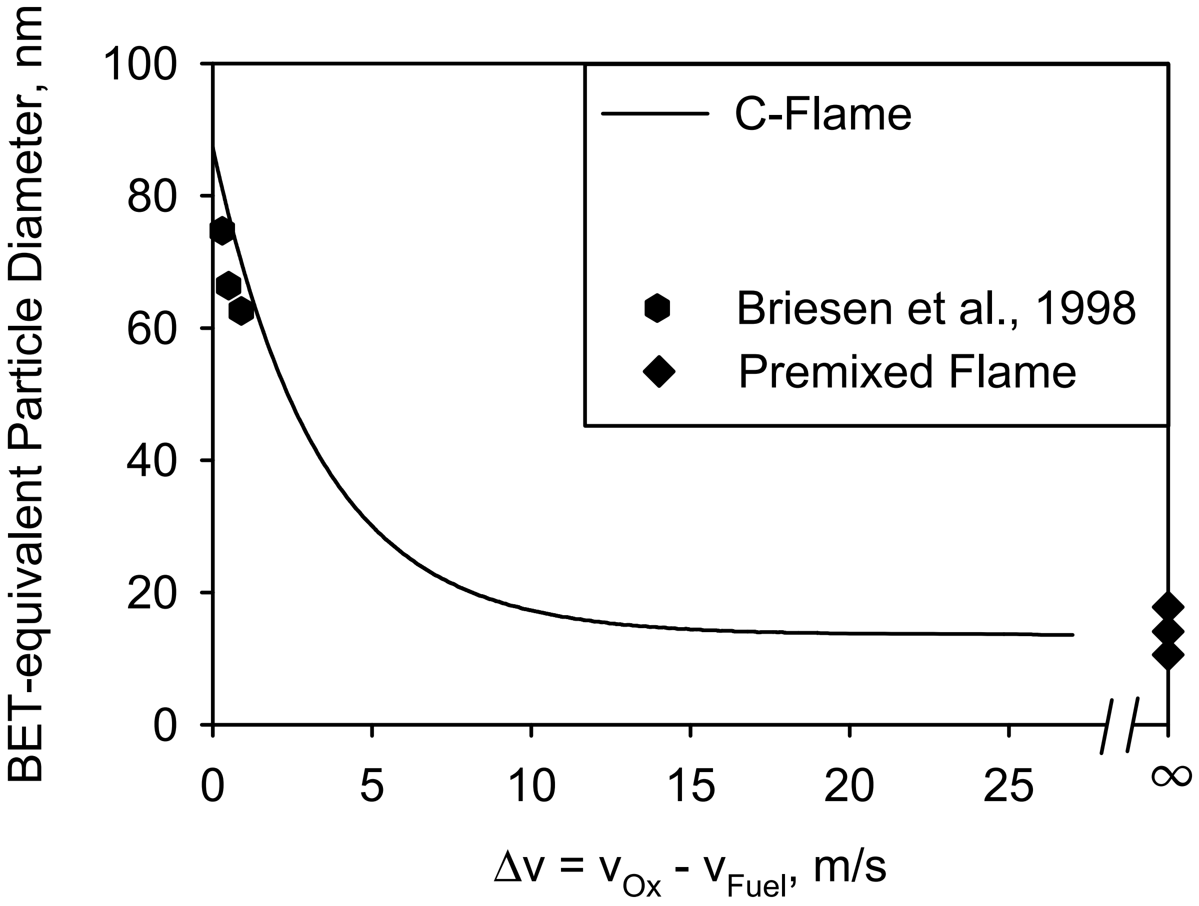
Operation Line for Silica synthesis

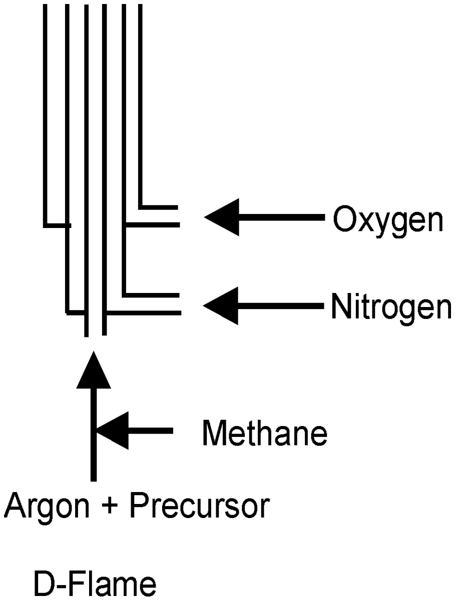


Operation Line for Silica synthesis

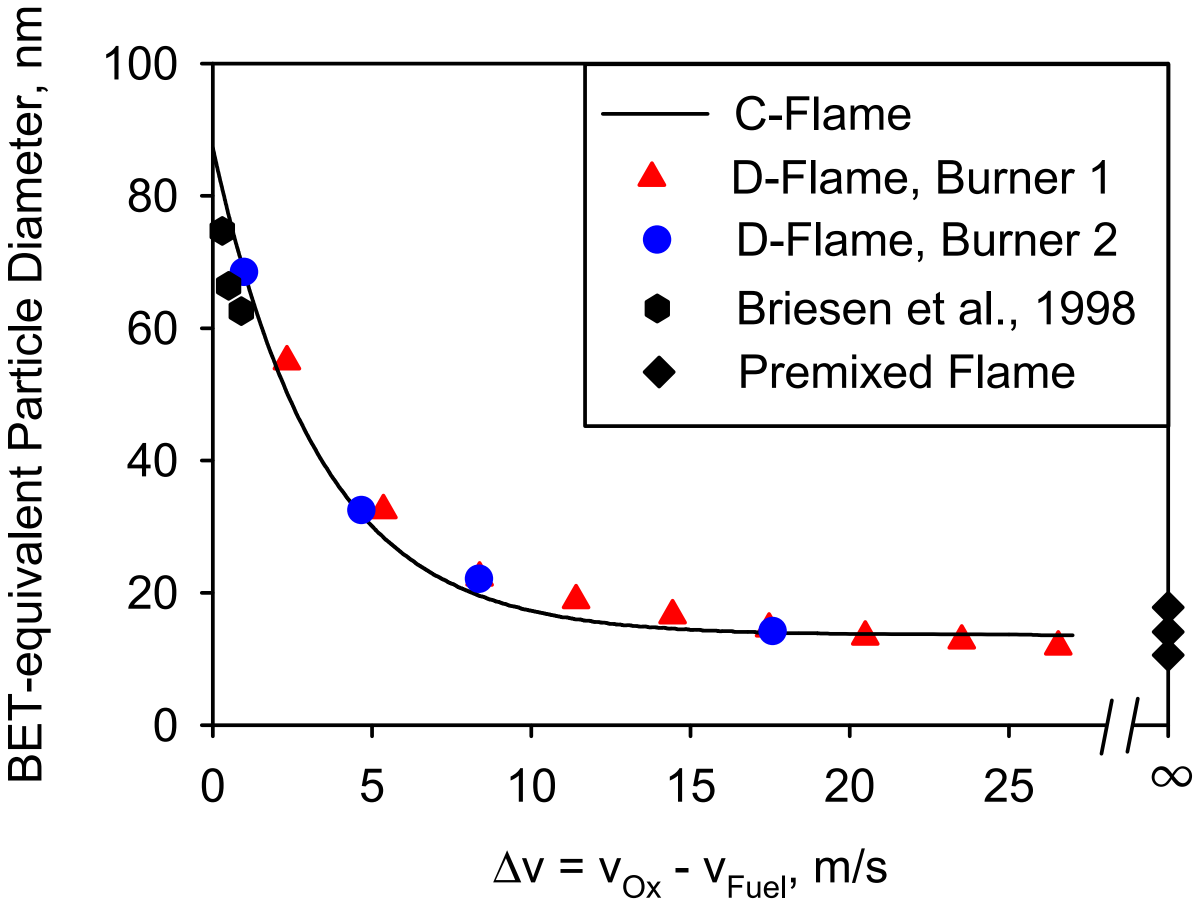


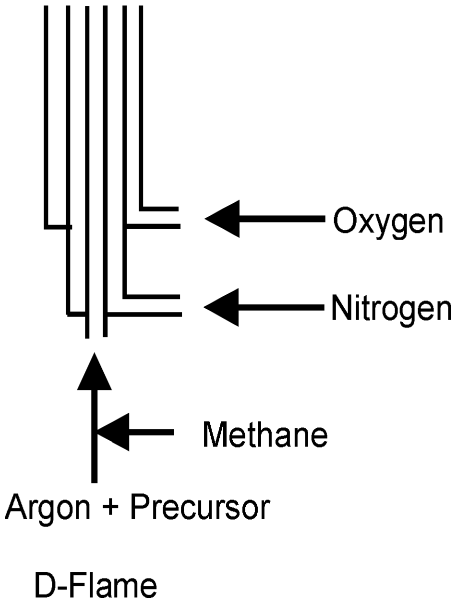
Operation Line for Silica synthesis





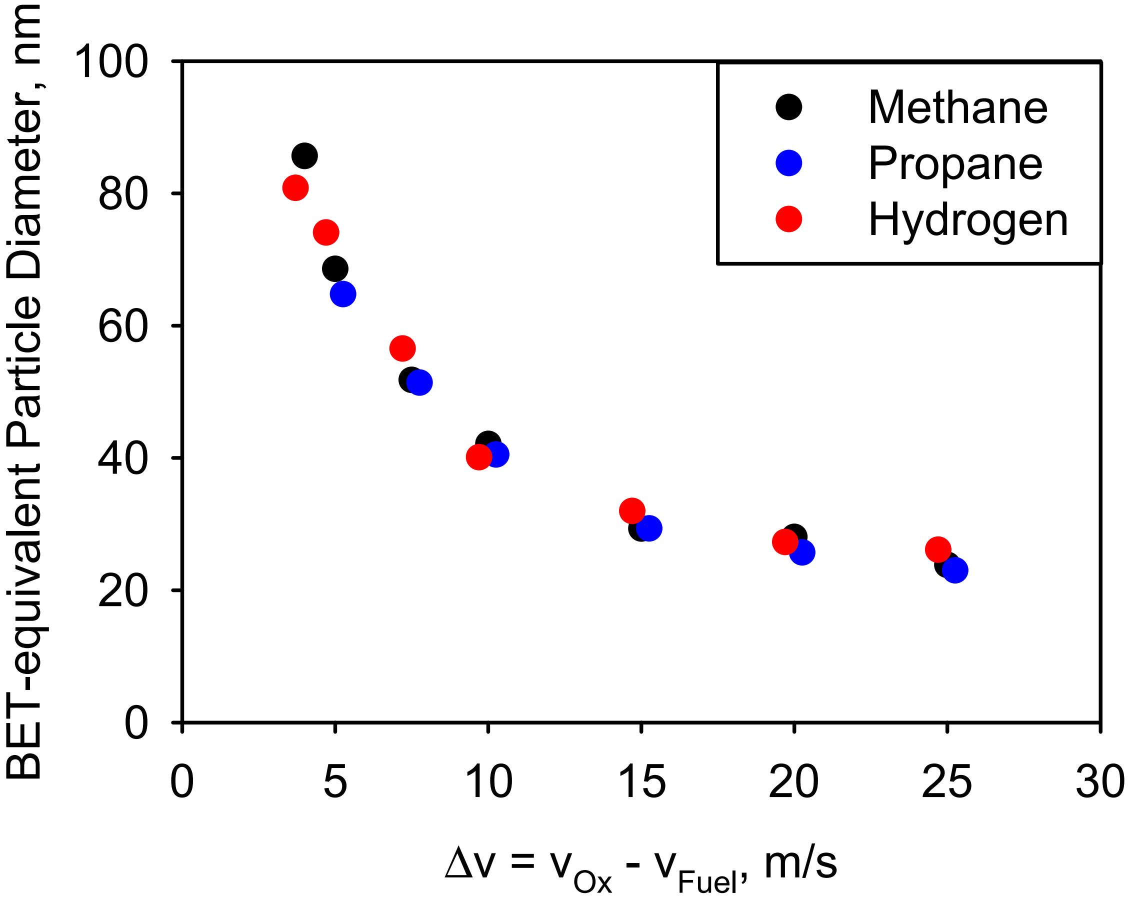
Operation Line for Silica synthesis



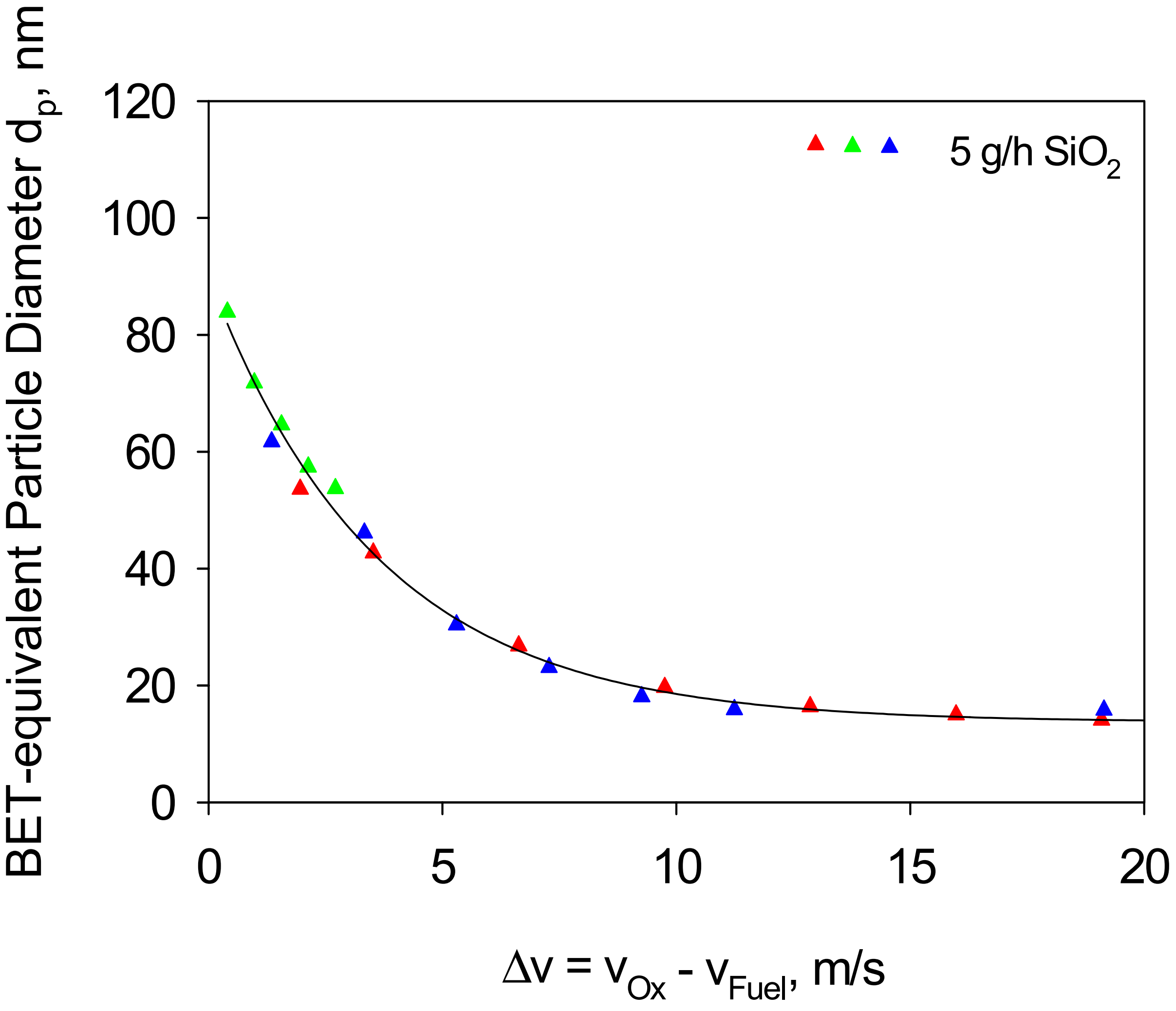


Different Fuels – Same Flame Enthalpy 25 g/h

SiO$_2$, 38 kJ/min by variation of fuel flow rate

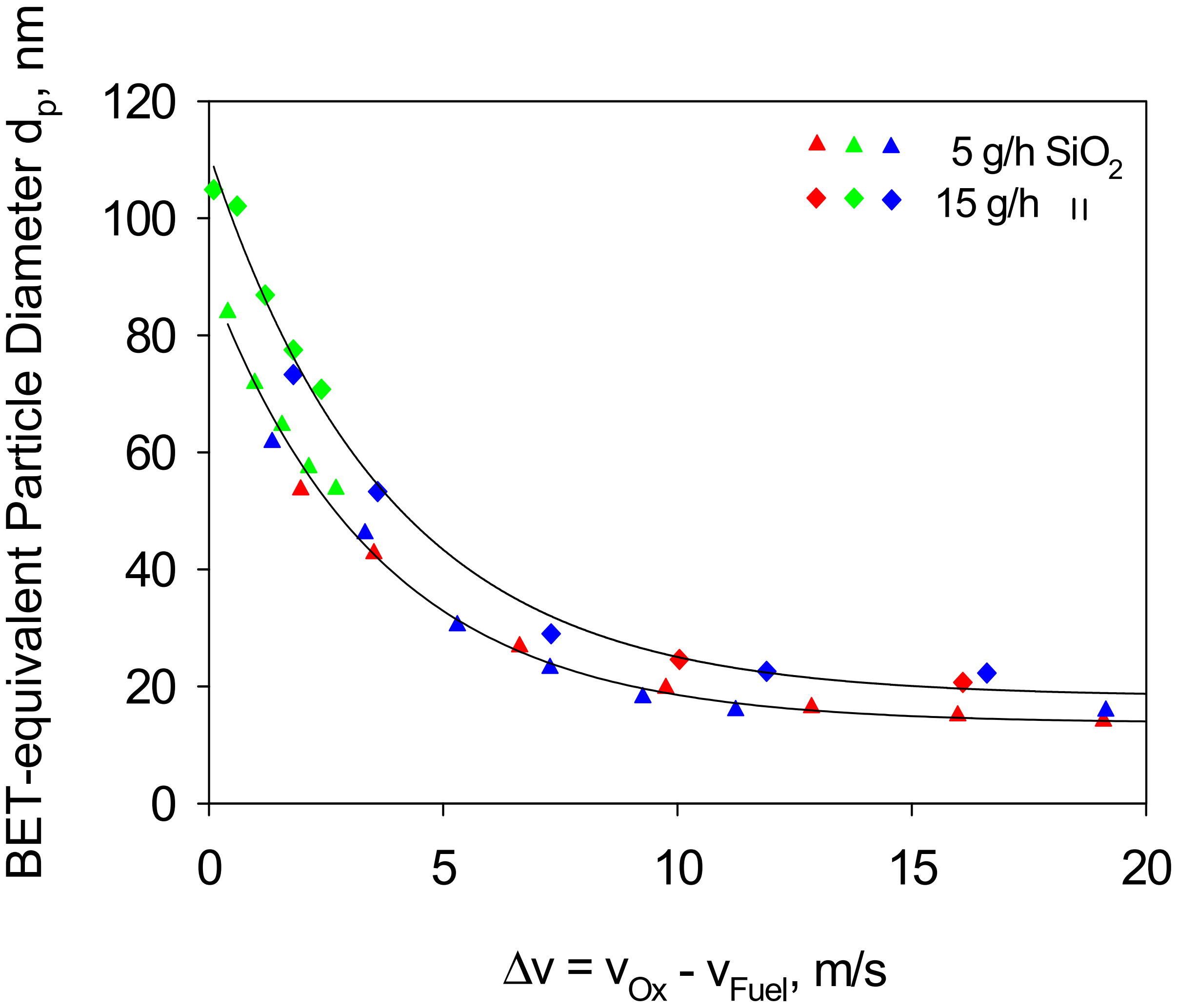


Production scale-up in the three burners



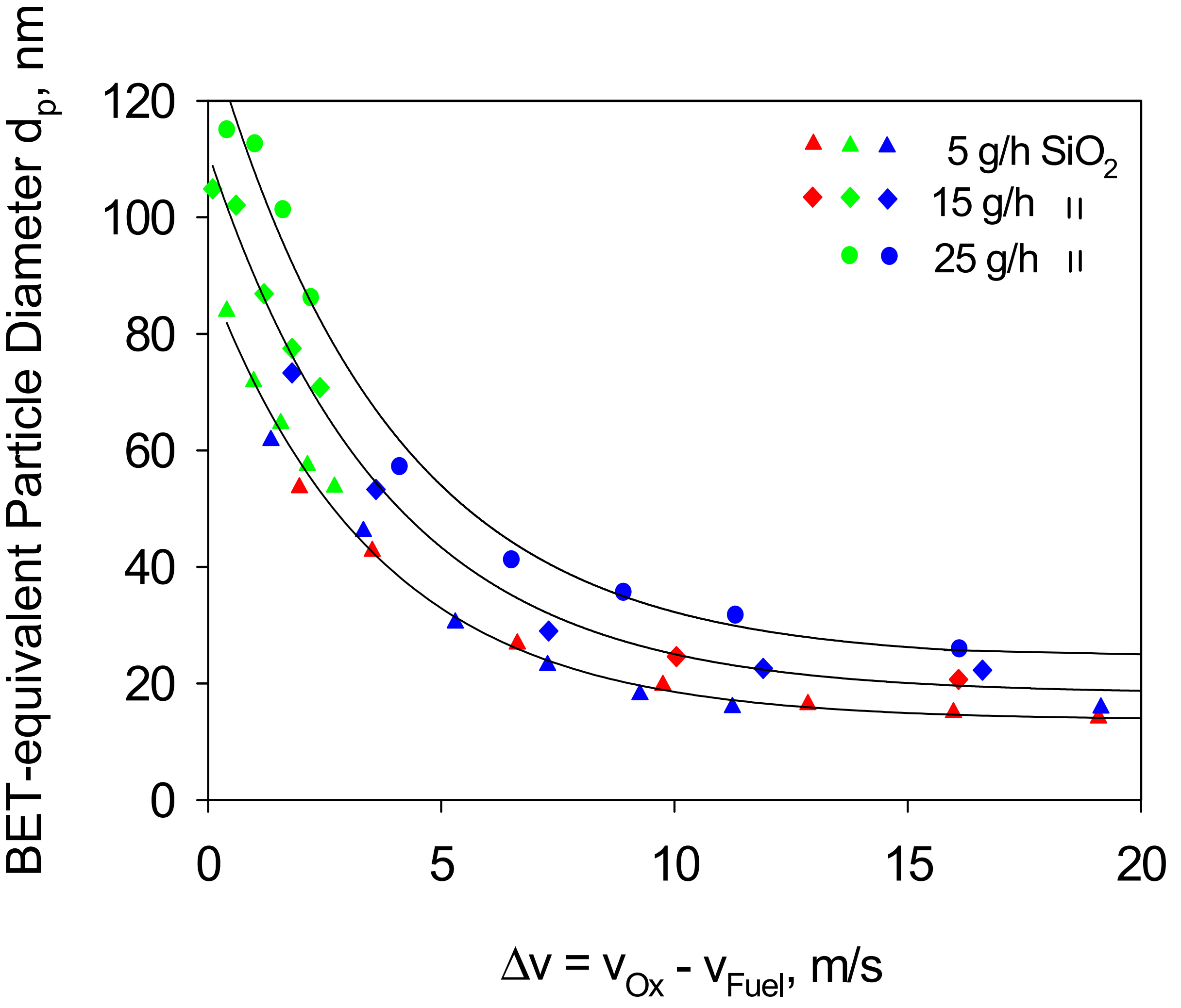
Increase of CH_4, Ar, and HMDSO flow rates

Production scale-up in the three burners



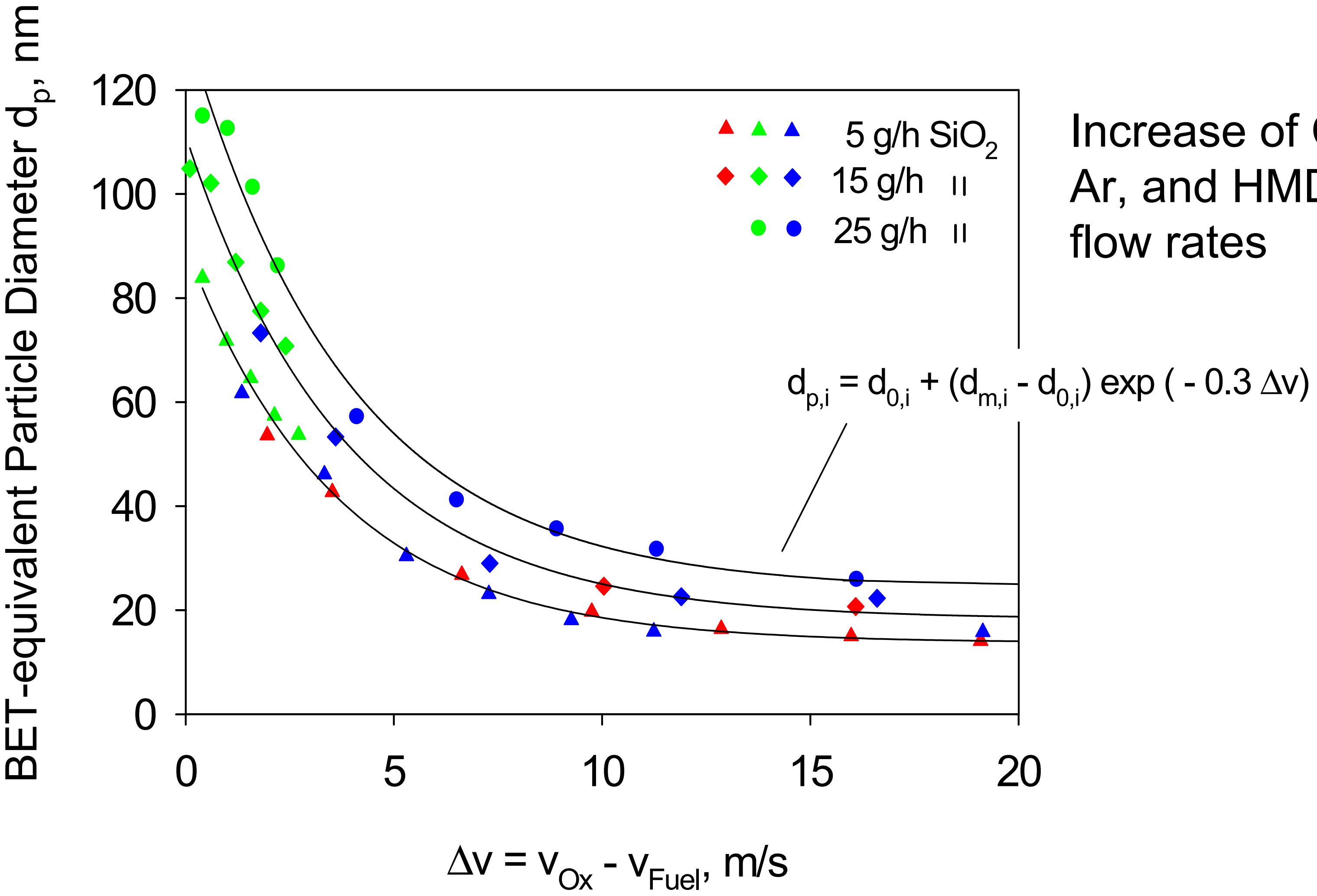
Increase of CH_4, Ar, and HMDSO flow rates

Production scale-up in the three burners



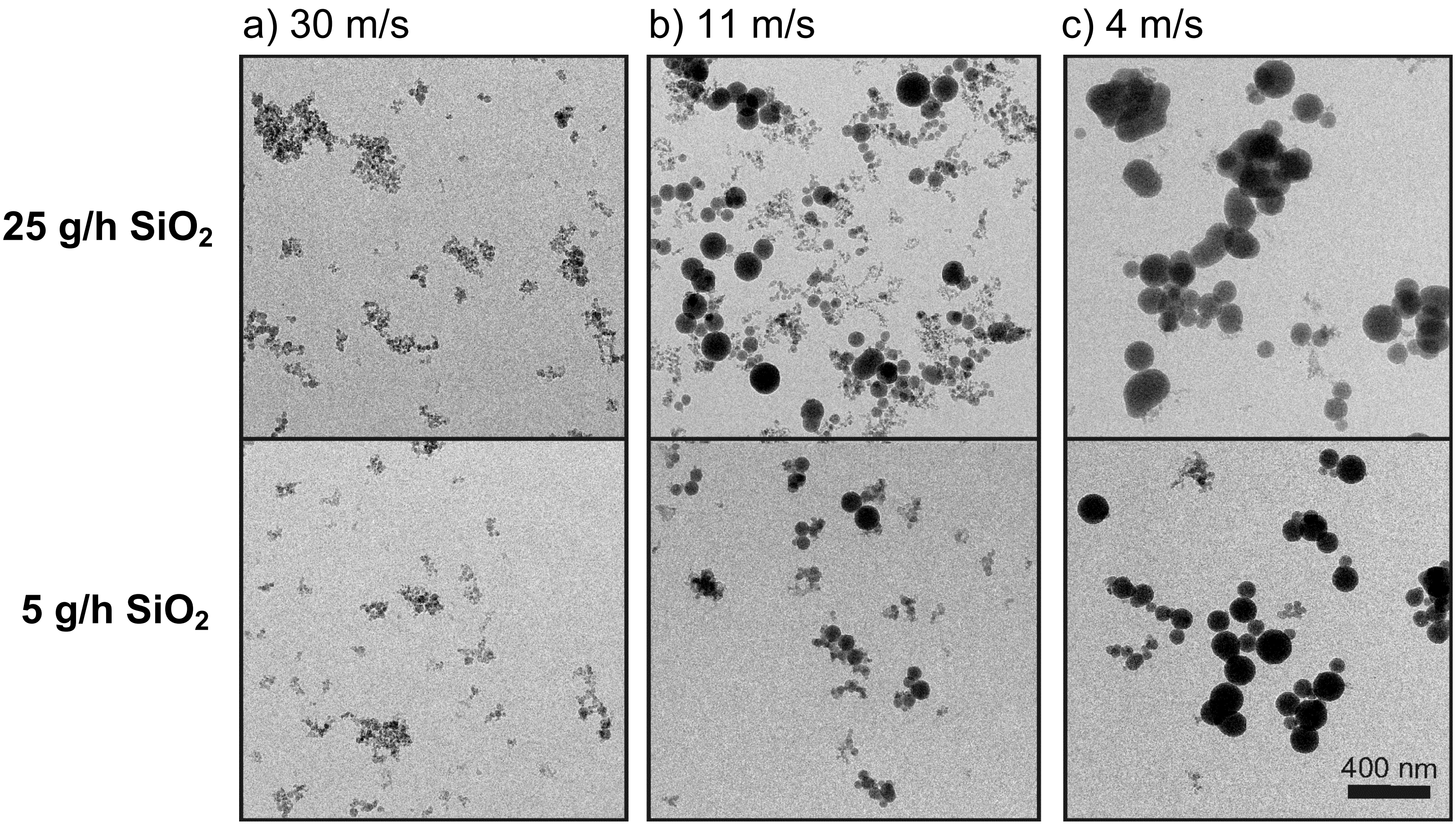
Increase of CH_4, Ar, and HMDSO flow rates

Production scale-up in the three burners



Increase of CH_4, Ar, and HMDSO flow rates

Particle Morphology Scale-up



a) 30 m/s

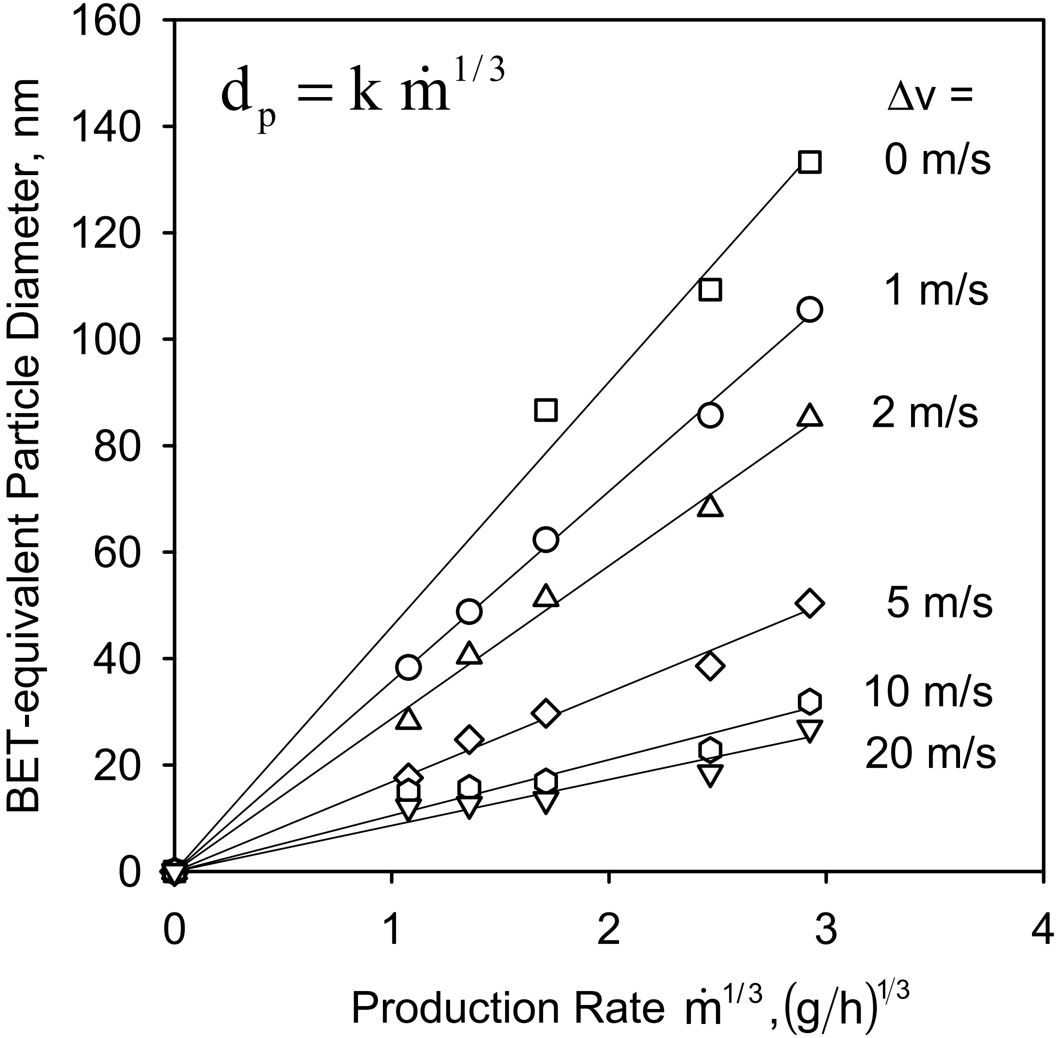
b) 11 m/s

c) 4 m/s

25 g/h SiO_2

5 g/h SiO_2

Scale-up Procedure



Δv = 0:

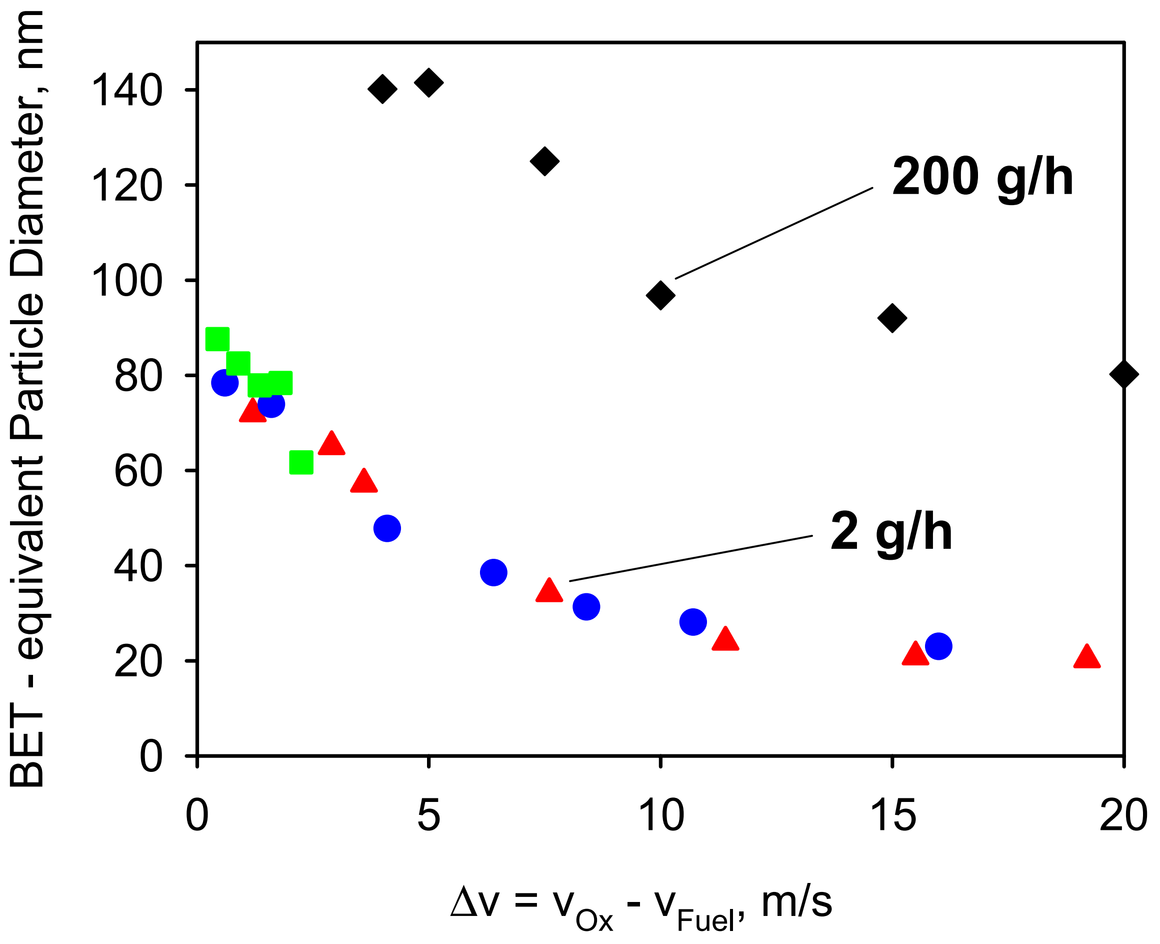
$$d_{m,i} = k_0\,\dot{m}_i^{1/3}$$

Δv → ∞:

$$d_{0,i} = k_\infty\,\dot{m}_i^{1/3}$$

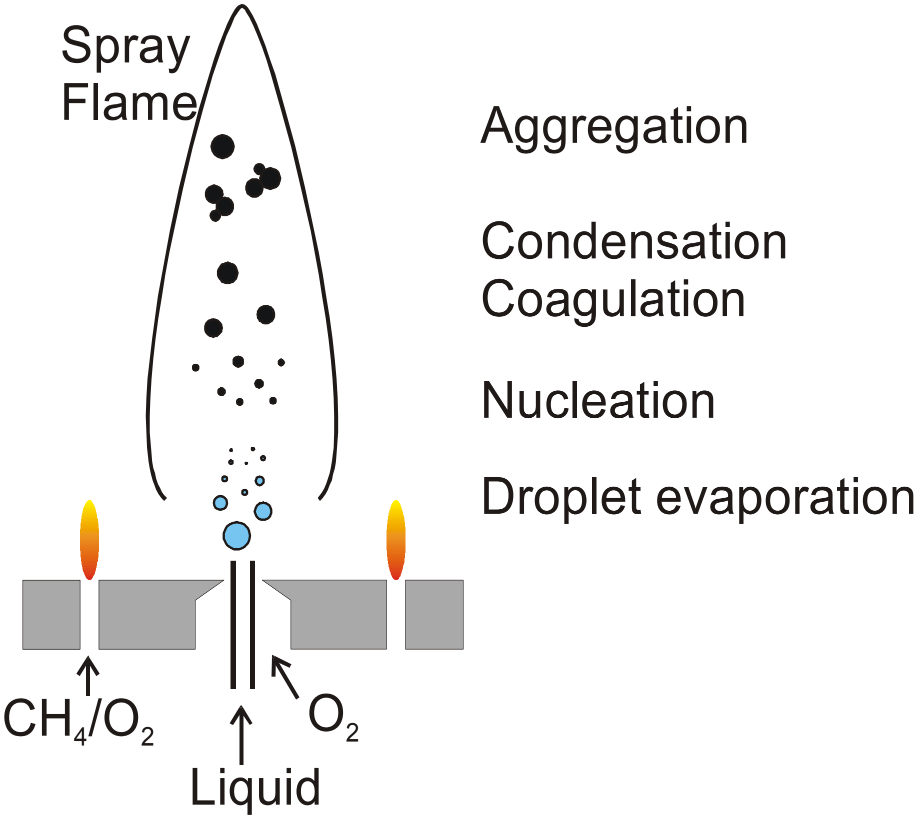
$$d_{p,i} = d_{0,i} + (d_{m,i} - d_{0,i}) \times \exp(-0.3\,\Delta v)$$

Scale-up of Titania Flame Synthesis



Flame Spray Pyrolysis (FSP)

- **versatile**
- **large variety of precursors**
- **controllable**
- **scaleable**



Aggregation

Condensation
Coagulation

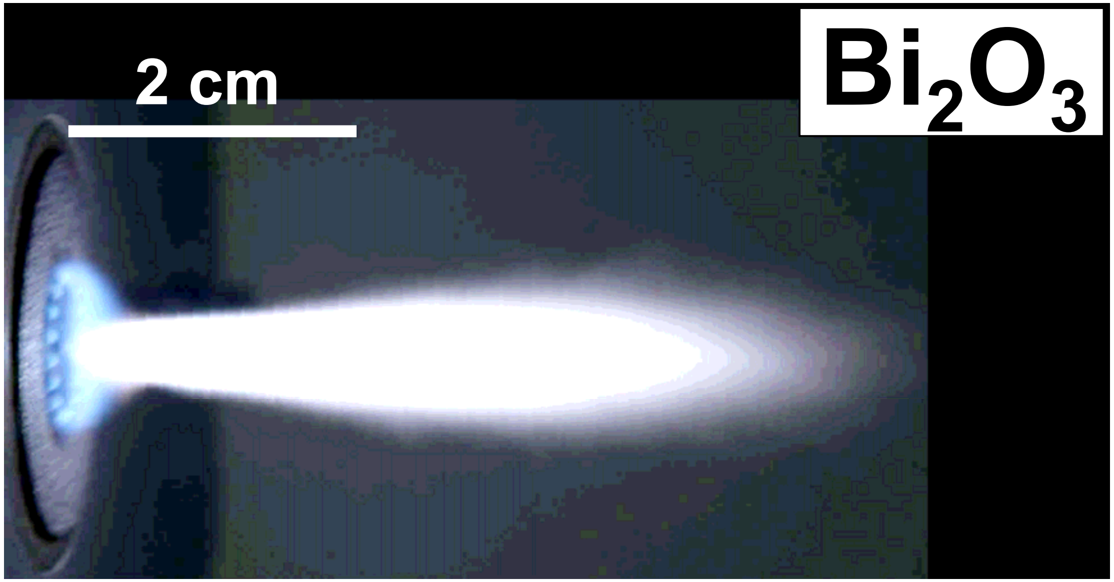
Nucleation

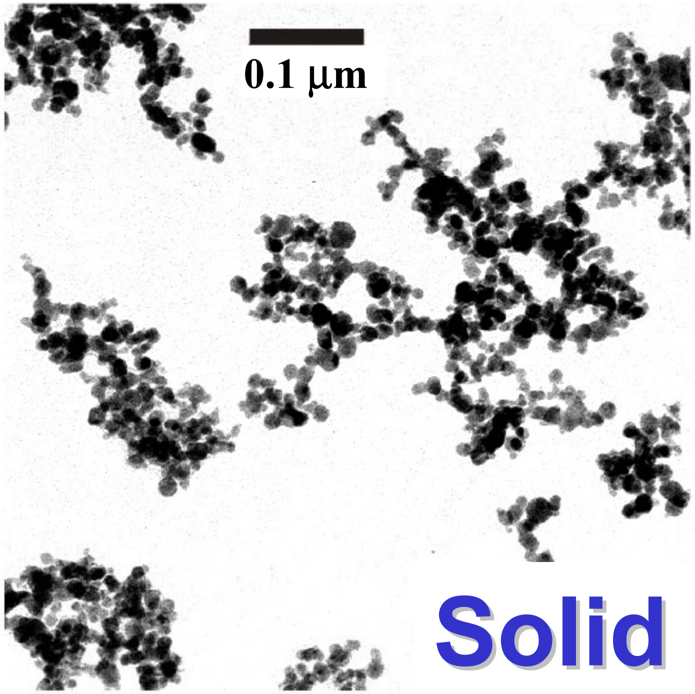
Droplet evaporation

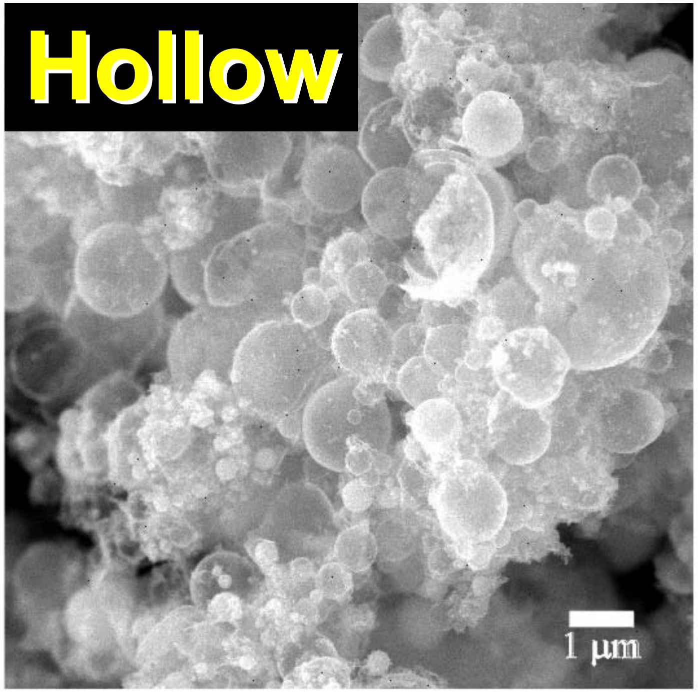
Mädler et al., *J. Aerosol Soc.* **33**, 369-389 (2002)

Flame Spray Pyrolysis

Al_2O_3, ZnO, CeO_2, ZrO_2
ZnO/SiO_2 , $BaTiO_3$
Au, Pt on TiO_2, SiO_2, Al_2O_3





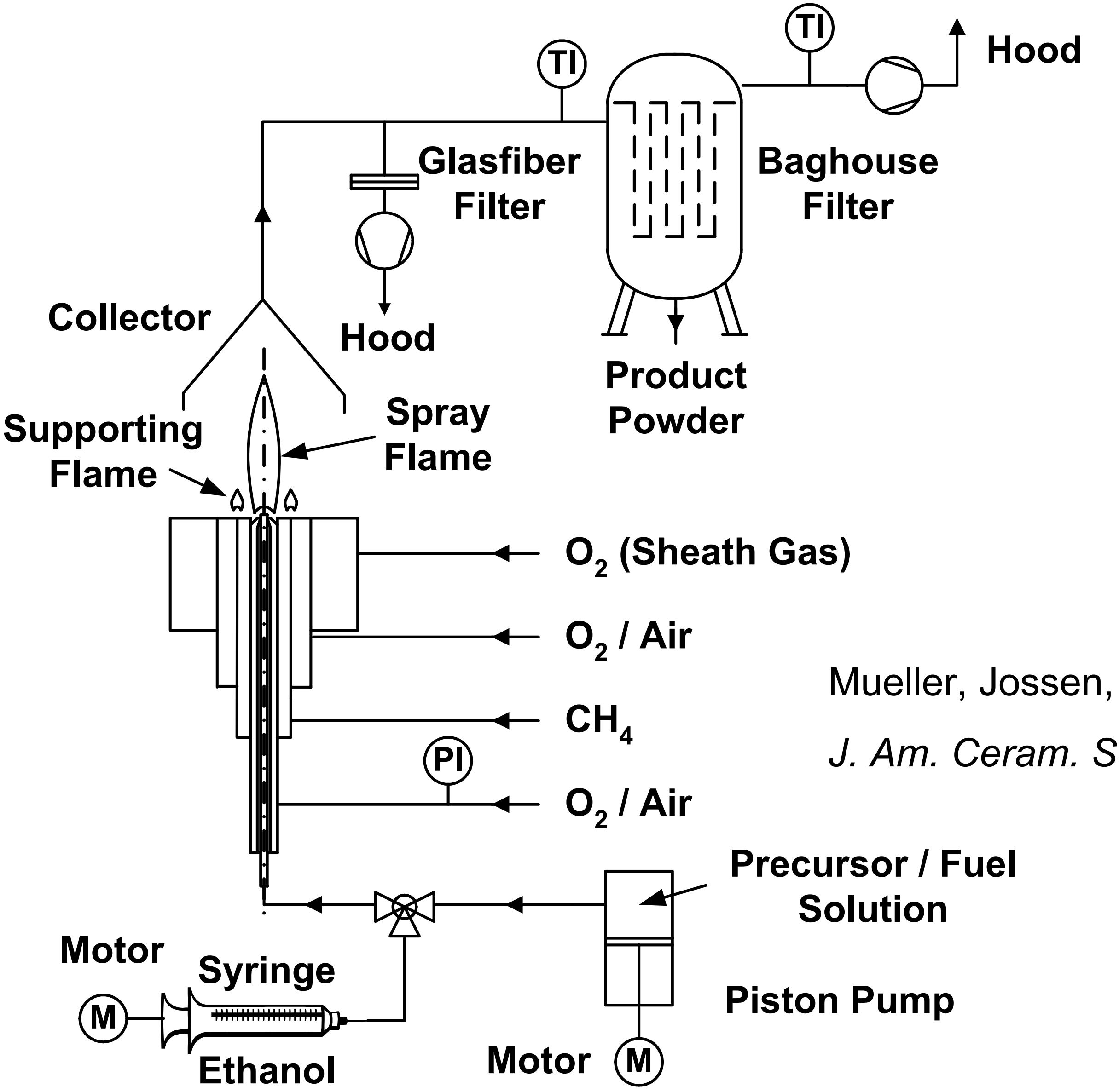


Mädler & Pratsinis, *J. Am. Ceram. Soc.* **85,** 1713-8 (2002)

Varistors
Sensors
Catalysts

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

FSP: Fundamentals of Scale-up

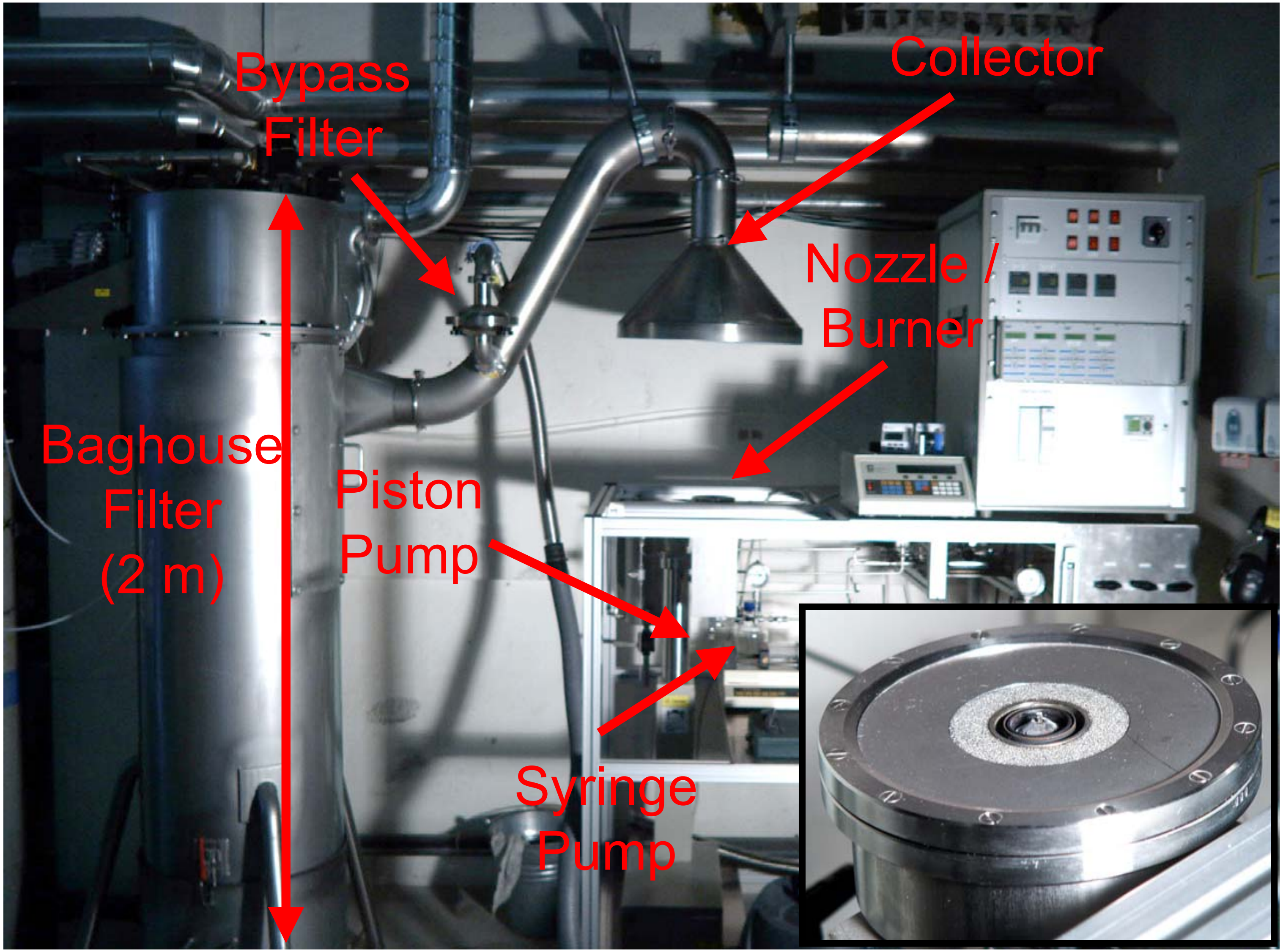


Mueller, Jossen, Pratsinis, Watson, Akhtar

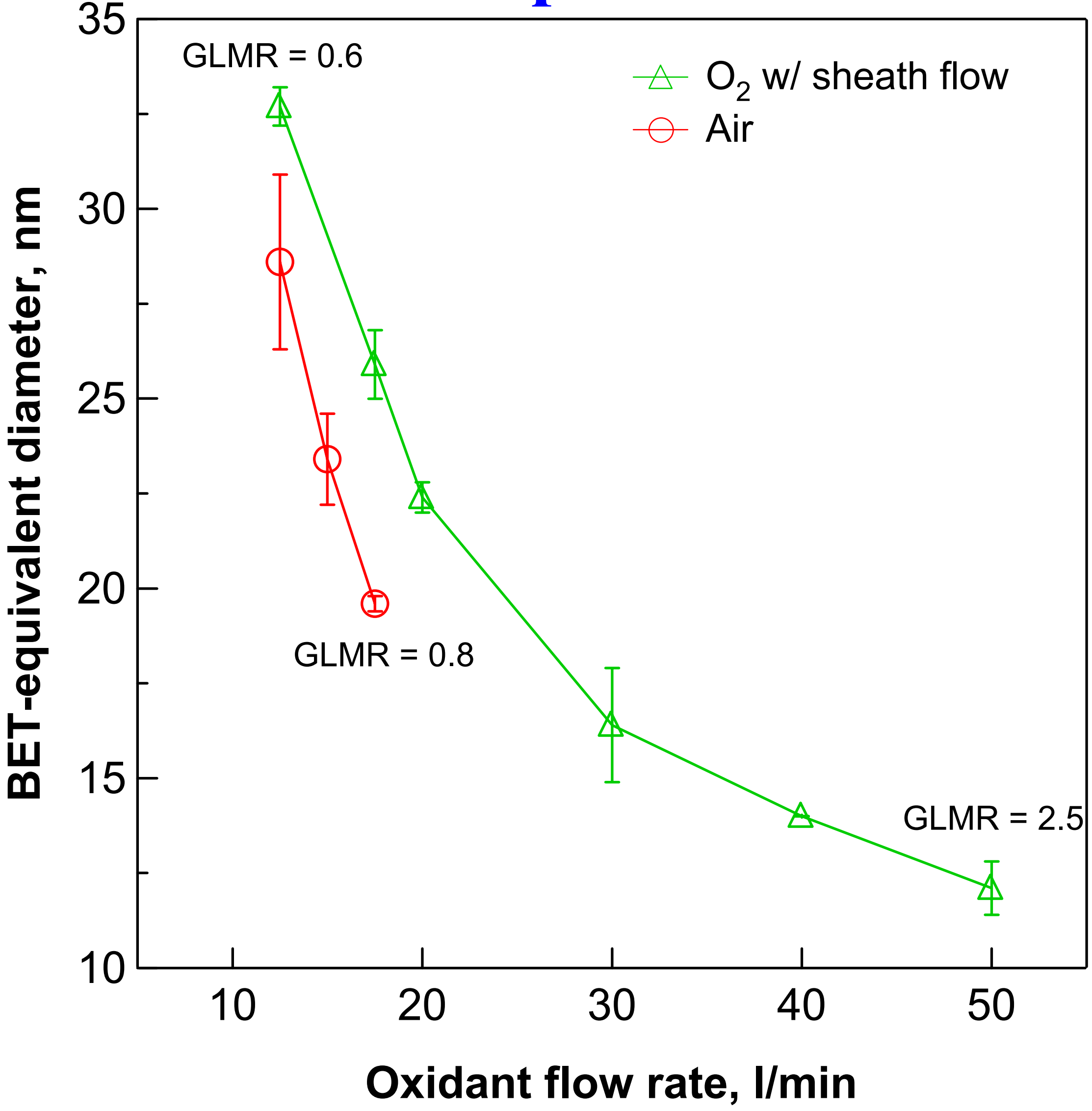
J. Am. Ceram. Soc., **87**, 197-204 (2004)

Experimental Set-up

Mueller, Jossen, Pratsinis, Watson, Akhtar, *J. Am. Ceram. Soc.*, **87** (2), 197-202 (2004)



FSP: Oxidant Flow Rate on SiO_2 primary particle diameter

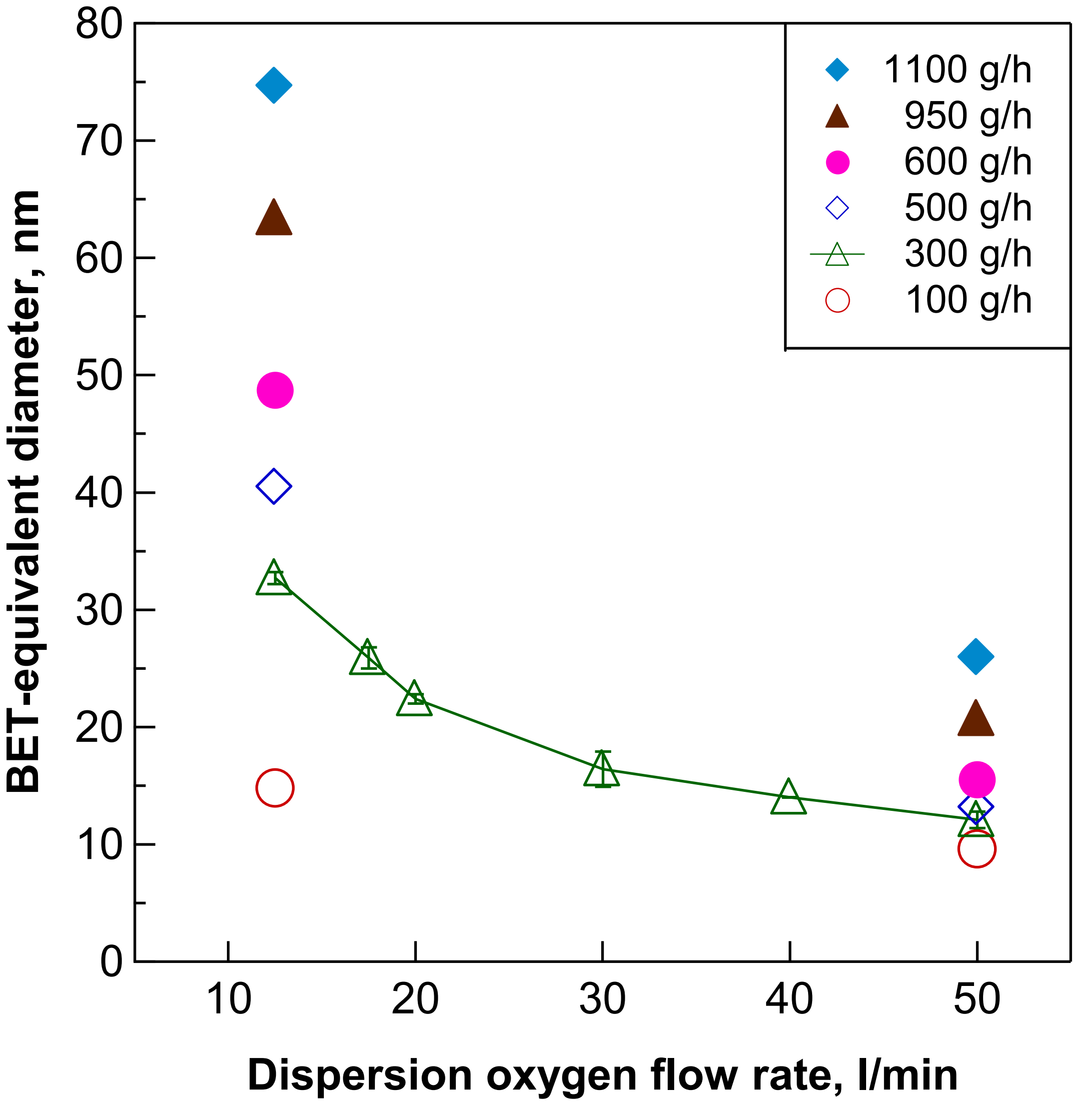


1.26 M HMDSO in EtOH

Production rate 300 g/h

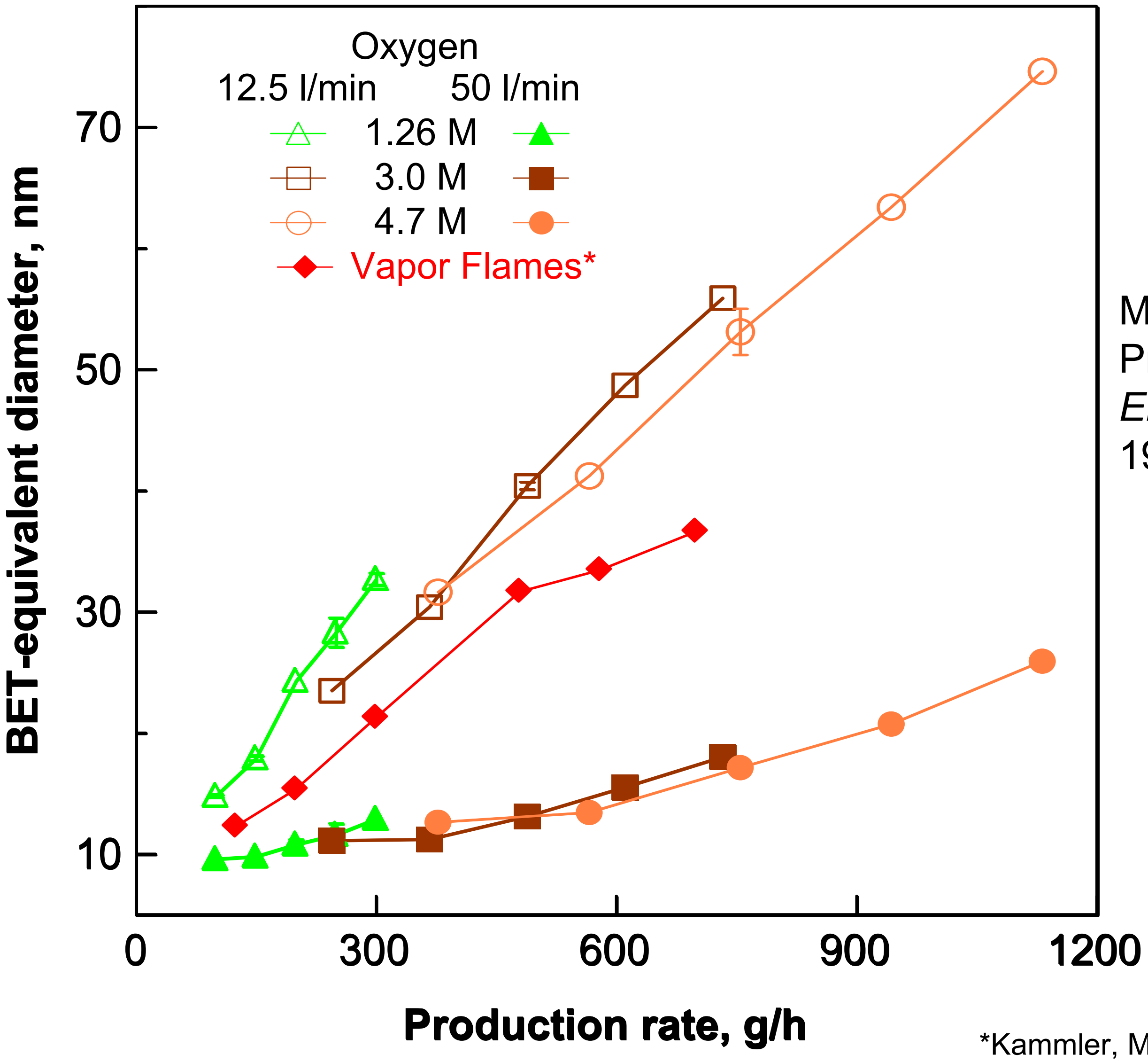
Mueller, Mädler, Pratsinis, *Chem. Eng. Sci.*, **58**, 1969-*76* (2003)

FSP: Oxidant Flow Rate on SiO_2 primary particle diameter



Mueller, Mädler,
Pratsinis, *Chem.*
Eng. Sci., **58**,
1969-76 (2003)

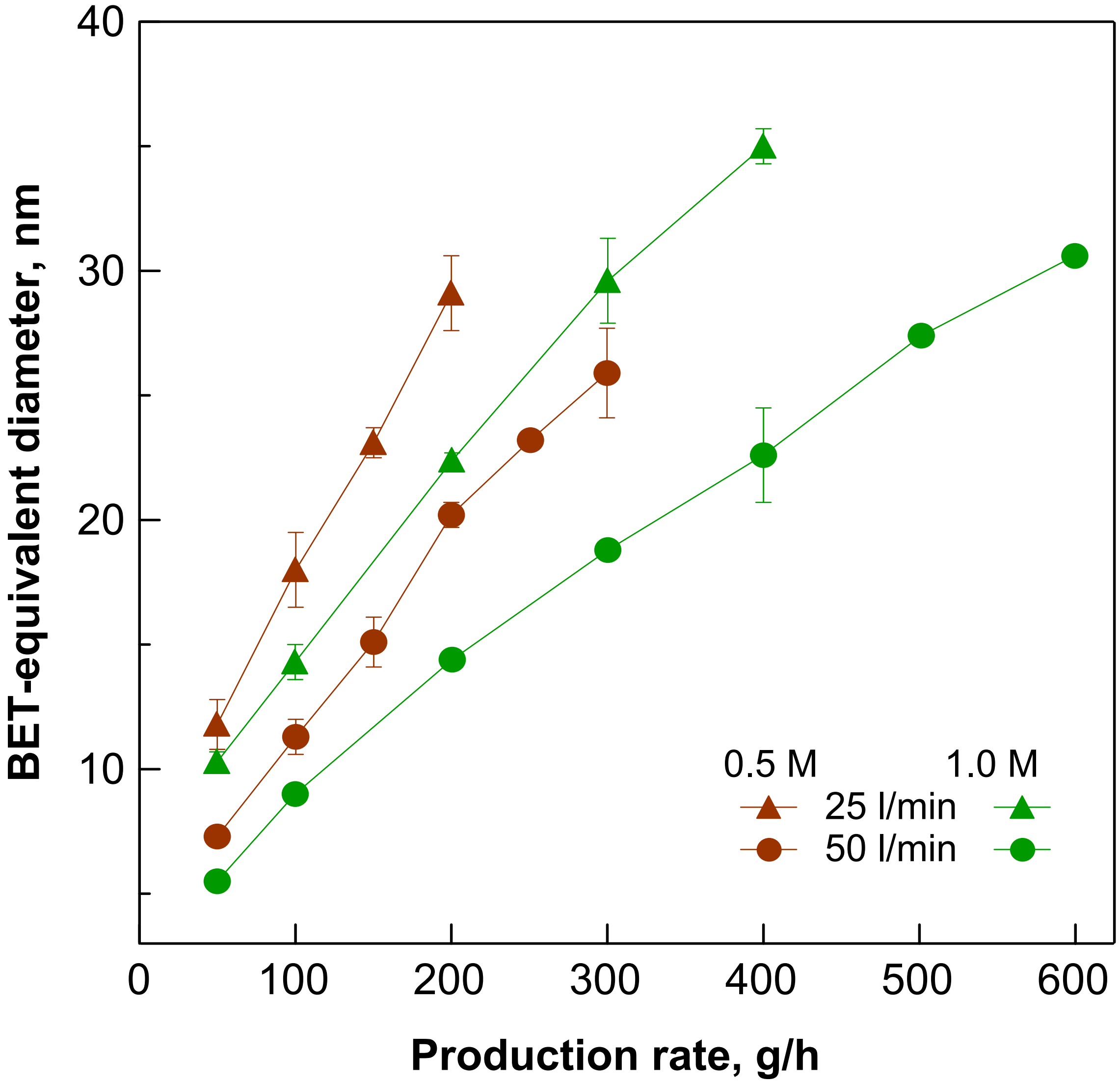
SiO_2 - Operation Window



Mueller, Mädler, Pratsinis, *Chem. Eng. Sci.*, **58**, 1969-*76* (2003)

*Kammler, Mueller, Senn, Pratsinis, *AIChE J.*, **47**, 1553-1543 (2001)

ZrO_2 - Operation Window



Mueller, Jossen,
Pratsinis, Watson,
Akhtar,
J. Am. Ceram. Soc.,
87, 197-202 (2004).

Conclusions

- Existing vapor-fed flame reactors can be scaled by computational fluid and particle dynamic simulations.
- The reactant outlet velocity difference determines product characteristics → One operation line for different burners.
- At large velocity difference, the performance of a diffusion flame converges to that of an equivalent premixed flame.
- Scale-up correlations were developed for flexible diffusion flame reactors and tested for SiO_2 & TiO_2 n-p (2-200 g/h).
- Liquid-fed flame reactors follow closely the above in synthesis of solid, non-hollow pure and mixed ceramic oxide particles.