Fundamentals of Particle Formation

Dr. Frank Ernst

ernst@ptl.mavt.ethz.ch
phone: 044 632 25 10

Office hour:
Thursdays after the lecture

Department of Mechanical and Process Engineering
ETH Zurich, www.ptl.ethz.ch
Lecture outline

- Revisited flames from a materials perspective
- Examples of flame-made materials
- Key processes of particle formation in flames
Flames revisited

**Combustion:**

- Rapid chemical reaction between fuel and oxidant releasing heat

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{energy}
\]
Flames revisited

**Combustion:**
- Rapid chemical reaction between fuel and oxidant releasing heat

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{energy} \]

**Flame:**
- Luminous zone formed by combustion of fuel and oxidant
Flames revisited

Basic flame types:

- **Premixed**
  - Laminar
  - Turbulent

- **Diffusion** (non-premixed)
  - Laminar
  - Turbulent

**Fuel / oxidiser mixing**

**Fluid motion**

**Examples**

- Flat flame
- Spark ignition engine
- Candle
- Pulverised coal combustor
Combustion is a chemical reaction

\[ A + B \xrightarrow{- \text{heat}} C + D \]

Air or \( \text{O}_2 \) can be used with HC to produce:

- For high temperature supply (e.g. cement production):
  \[ \text{CO}_2/\text{CO} + \text{H}_2\text{O} + \text{NO}_x + \text{C} + \text{HC} \]
- For material production:
  \[ \text{CO}_2 + \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 + \ldots \]
  \[ \text{C(s)} + \text{CO} + \text{H}_2\text{O} \]

utilize **heat** for high temperature supply (e.g. cement production) utilize **chemical reaction** and **heat** for material production
Flames revisited

Contacting fuel/oxygen & chemical reaction

Chemical reactions kinetics & thermodynamics

Temperature

Fluid flow Laminar & turbulent

Combustion science:
- Focus on energy and gaseous species formation
- Particle and material formation focus often environmental eg. Soot
- Flames are also useful to make many interesting and commercial materials
Materials produced in flames

1. Gas Production:

   HCl, C₂H₂, O₂, N₂, SO₂ (H₂SO₄), P₂O₅ (H₃PO₄)

2. Solid Manufacture and Processing
   (Welding; Cutting with C₂H₂/O₂ torches etc.)

   Particles (carbon black, TiO₂, SiO₂, Al₂O₃)

   Films or Coatings (light-guides, ceramics: thermal sprays)
Why materials?

- Materials are used in every aspect of society
- Particulate materials (e.g., Powders) are used in large volumes and for many different applications
- Some examples...
# Solids manufacture – in flames

<table>
<thead>
<tr>
<th>Established Product Particles</th>
<th>Volume t/y</th>
<th>Ind. Process (dominant)</th>
<th>Use (exemplary)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td>8 M</td>
<td>Spray Flame</td>
<td>Inks, tires</td>
</tr>
<tr>
<td>Titania</td>
<td>2 M</td>
<td>Vapor Flame</td>
<td>Paints</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>0.2 M</td>
<td>Vapor Flame</td>
<td>Toothpaste, flowaid</td>
</tr>
</tbody>
</table>

PROMISING: Catalysts, Sensors, Photonics, Biomaterials

Carbon black
Channel Plant, Texas Panhandle, 1940's

Columbian Chemicals, 1994

Degussa, 1996
Furnace black process

Furnace
- oil
- gas
- water
- air

Separation
- heat recovery
- baghouse
- cyclone
- Tail gas (energy recovery)

Product
- Exhaust air
- Fluffy carbon black
- Pellet carbon black
- storage

Furnace Process:

Carbon Black by Spray combustion
Silica (SiO$_2$)
Hydrogen
Oxygen (air)
Silicon tetrachloride
vaporizer
mixing
burner
cooling
Filters
and/or
cyclone
HCl absorption
de-acidification
Fumed silica

Deposition of Films or Coatings - Optical Fibers

Transmit light over very long distance

Requirements:
- high purity
- controlled refractive index

Rowell (1986)
Titania (TiO$_2$)
Titania Pigments ($\text{TiO}_2$)

Chloride Process

- Ore
- Rutile
- Ilmenite
- Reaction Purification
- $\text{TiCl}_4$
- Oxidation
- $\text{Cl}_2$
- TiO$_2$ Powder
- Finishing
- Paint

Rutile Content
Hiding Power
Gloss
CBU
Durability
Dispersion
Leveling
Brushing
etc.
Why flames to make particles?

The flame is the reactor!

- high mobility of reactants and particles
- highly reactive environment
- high heat and mass transfer
- Rapid synthesis. $O(10)$ to $O(100)$ milliseconds
- Easily up-scaled from gram to tonne scale

For material synthesis we want to increase amount of particles formed and control their properties
Particle formation

- Product particles are a solid material with sizes up to microns (μm)
- Fixed chemical composition
  - Eg. TiO$_2$, SiO$_2$, C, Al$_2$O$_3$
- Growth proceeds by joining together of small molecular-scale units

molecules $\rightarrow$ particles
Particle formation & growth

Chemical reactions
kinetics & thermodynamics

Temperature

Fluid flow
Laminar & turbulent

Source of molecular building unit “monomer”

eg. $\text{TiCl}_4 + 2\text{O}_2 \rightarrow \text{TiO}_2 + \text{Cl}_2$

Environment supporting particle growth

$\text{TiO}_2$ $\text{TiO}_2$

$\text{TiO}_2$ $\text{TiO}_2$

$\text{TiO}_2$ $\text{TiO}_2$
Particle formation & growth – key steps

Chemical Reaction:
Gas-phase chemical reactions are source of monomer species.

\[
\begin{align*}
\text{TiCl}_4 + \text{O}_2 & \rightarrow \text{TiO}_2 + 2\text{Cl}_2 \\
\text{SiCl}_4 + \text{O}_2 & \rightarrow \text{SiO}_2 + 2\text{Cl}_2 \\
\text{C}_2\text{H}_2 + k\text{O}_2 & \rightarrow 2(1-k)\text{C} + 2k\text{CO} + \text{H}_2
\end{align*}
\]
Particle formation & growth – key steps

Chemical reaction

Chemical Reaction:
Gas-phase chemical reactions are source of monomer species.

\[
\begin{align*}
\text{TiCl}_4 + \text{O}_2 & \rightarrow \text{TiO}_2 + 2\text{Cl}_2 \\
\text{SiCl}_4 + \text{O}_2 & \rightarrow \text{SiO}_2 + 2\text{Cl}_2 \\
\text{C}_2\text{H}_2 + k\text{O}_2 & \rightarrow 2(1-k)\text{C} + 2k\text{CO} + \text{H}_2
\end{align*}
\]

First-order consumption of precursor
eg. C is concentration of TiCl_4

\[
\frac{dC}{dt} = -kC
\]

\[
C = C_o \exp(-kt)
\]

where \( C_o \) is initial precursor concentration

Particle formation & growth – key steps

**Nucleation:**
Formation of initial clusters

1. **Homogenous nucleation:** equilibrium between condensation and evaporation
2. **Coagulation:** If monomer is thermodynamically stable the monomer molecule is the critical cluster
   - *This is generally the case for metal oxide systems*
**Particle formation & growth – key steps**

- **Chemical reaction**
- **Nucleation**
- **Coagulation**

Coagulation:
Collisions between clusters, monomers and other particles leads to larger particles

Average velocity ($u$) of molecules and small particles

\[ u = \left( \frac{8k_B T}{\pi m} \right)^{\frac{1}{2}} \]

\( k_B \) = Boltzmann constant
\( m \) = Particle mass
Particle formation & growth – key steps

Chemical reaction

Nucleation

Coagulation

Coagulation:
Collisions between clusters, monomers and other particles leads to larger particles

\[ u = \left( \frac{8k_B T}{\pi m} \right)^{1/2} \]

\[ k_B = \text{Boltzmann constant} \]
\[ m = \text{Particle mass} \]
Coagulation

- *Collisions* and *coalescence* of particles gives fewer but larger particles

- Dynamics of particle growth related to
  - Velocity of particles (Temperature, mass)
  - Probability of collision (Concentration, size)
Idealized case – Monodisperse coagulation

- **Monodisperse** = all particles have the same size
- Assume here that all particles stay **same size** despite collisions (strong but useful assumption!)
- We only consider the **total number concentration**
  
  (# particles per unit volume)
Idealized case – Monodisperse coagulation

Rate of change of number concentration

\[ \frac{dN}{dt} = -\frac{1}{2} \beta (v_1, v_1) N^2 \]

where \( \beta = \frac{2k_B T}{3\mu} \left( \frac{1}{v_1^{1/3}} + \frac{1}{v_1^{1/3}} \right) \left( v_1^{1/3} + v_1^{1/3} \right) = \frac{8k_B T}{3\mu} \) (continuous regime)

then

\[ \frac{dN}{dt} = -\frac{\beta}{2} N^2 \]

integration

\[ N = N_o \left(1 + \frac{\beta N_o}{2} t\right)^{-1} \]

monodisperse same sized

\[ N = \# \text{ particles per volume} \]
\[ \beta= \text{Collision frequency function} \]
\[ (rate \text{ of collisions per particle per volume}) \]
\[ v = \text{particle volume} \]
Coagulation

- More correctly, for true coagulation the number of particles decreases and the average particle size increases.
- We consider the number concentration of each particle size (# particles per unit volume).
Coagulation

Consider $n_k$ to be the number concentration of particles of size $k$.

**Birth** of particles of size $k = i+j$ is:

$$\frac{1}{2} \sum_{k=i+j} \beta(v_i, v_j) n_i n_j$$

($\frac{1}{2}$ factor corrects for double counting)

**Loss** of particles of size $k$ by collision with other particles:

$$\sum_{i=1}^{\infty} \beta(v_k, v_i) n_k n_i$$

Then net rate of change in particle concentration is:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{k=i+j} \beta(v_i, v_j) n_i n_j - \sum_{i=1}^{\infty} \beta(v_k, v_i) n_k n_i$$

*polydisperse*
Coagulation

\[
\frac{dn_k}{dt} = \frac{1}{2} \sum_{k=i+j} \beta(v_i, v_j) n_i n_j - \sum_{i=1}^{\infty} \beta(v_k, v_i) n_k n_i
\]
Motion in Gases

- Air molecules are in continuous motion
- They collide among themselves because of their translational energy
- The translational energy is proportional to the air temperature
Gas mean free path

The average distance traveled by gas molecules is called the mean free path ($\lambda$):

$$\lambda = \frac{2 \mu}{\rho u}$$

where

$$u = \left( \frac{8 k_B T}{\pi m} \right)^{\frac{1}{2}}$$

$\mu = \text{dynamic viscosity}$

$\rho = \text{density}$
## Properties of Air

<table>
<thead>
<tr>
<th>Distance</th>
<th>Length\textsuperscript{\textmu m}</th>
<th>Ratio to Molecular Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular diameter</td>
<td>0.00037</td>
<td>1</td>
</tr>
<tr>
<td>Approximate molecular spacing</td>
<td>0.004</td>
<td>10</td>
</tr>
<tr>
<td>Mean free path</td>
<td>0.066</td>
<td>180</td>
</tr>
<tr>
<td>0.1-\textmu m particle</td>
<td>0.1</td>
<td>260</td>
</tr>
</tbody>
</table>

Coagulation

- For atmospheric T and P, \( \lambda \) is typically \( O(100 \text{ nm}) \)
- The ratio of the mean free path to the particle size \( (d_p) \) is the Knudsen number \( (Kn) \):
  \[
  Kn = \frac{2 \lambda}{d_p}
  \]
  - \( Kn >> 1 \): Free Molecular Regime
  - \( Kn \sim 1 \): Transition Regime
  - \( Kn << 1 \): Continuum Regime
- Particles smaller than the mean free path (ie. \( Kn > 1 \)) are in the Free-molecular regime
Coagulation in the Free Molecular Regime

- Collision frequency function ($\beta$) for free-molecular regime

$$\beta_{i,j} = \left( \frac{3}{4\pi} \right)^{1/6} \left( \frac{6k_BT}{\rho_p} \right)^{1/2} \left( \frac{1}{v_i} + \frac{1}{v_j} \right)^{1/2} \left( v_i^{1/3} + v_j^{1/3} \right)^2$$

- However, for particle growth in the free-molecular regime we can directly estimate the average diameter by:

$$d_p^{5/2} = d_{po}^{5/2} + \frac{10}{\pi} \left( \frac{6k_BT}{\rho_p} \right)^{1/2} \left( \frac{CM_P t}{\rho_p} \right)$$

Size as function of time but no information on distribution

---

Particle formation & growth – key steps

Chemical reaction | Nucleation | Coagulation | Aggregation

Aggregation:
- Occurs when particles are too large or T is too low for coalescent rearrangement
- Collisions leads to particle “chains”

1. Aggregates (“Hard agglomerates”): Particles strongly joined together
2. Agglomerates (“Soft agglomerates”): Weak forces. Particles easily separated
Particle formation & growth – key steps

Chemical reaction

Source of monomer species

Nucleation

Formation of clusters

Coagulation

Spherical particles form via particle-particle collisions

Aggregation

Collisions between spherical particles form chains

TiCl$_4$ + 2O$_2$ $\rightarrow$ TiO$_2$ + Cl$_2$

TiO$_2$

Decreasing number concentration

Increasing size and mass
Particle formation & growth – flames

Chemical reaction

Nucleation

Coagulation

Aggregation

T (K)

500 1000 1500 2000 2500

Particle formation & growth – flames

HCl
H₂O
TiO₂
TiCl₄
H₂
O₂

Chemical reaction

Nucleation

Coagulation

Aggregation

Particle formation & growth – flames

HCl
H₂O
TiO₂
TiCl₄
H₂
O₂

Chemical reaction

Nucleation

Coagulation

Aggregation
Lecture summary

- Revisited flames from a materials perspective
- Why materials are interesting. Examples of flame-made materials
- Key processes of particle formation in flames
  - Chemical reaction, nucleation, coagulation, aggregation
  - Coagulation: monodisperse and polydisperse
  - Coagulation: free-molecular and continuous regime

Further reading


