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Attrition of methanol to olefins catalyst in a jet cup

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Attrition of methanol to olefins catalyst in high temperature jet cup

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1、Background: MTO process

- MTO = methanol to olefins (ethylene and propylene)
  - world's first MTO commercial unit started up in 2010 by DICP
  - currently more than 10 units on stream
  - Turbulent fluidized bed reactor and bubbling fluidized bed regenerator
  - SAPO-34 zeolite catalyst

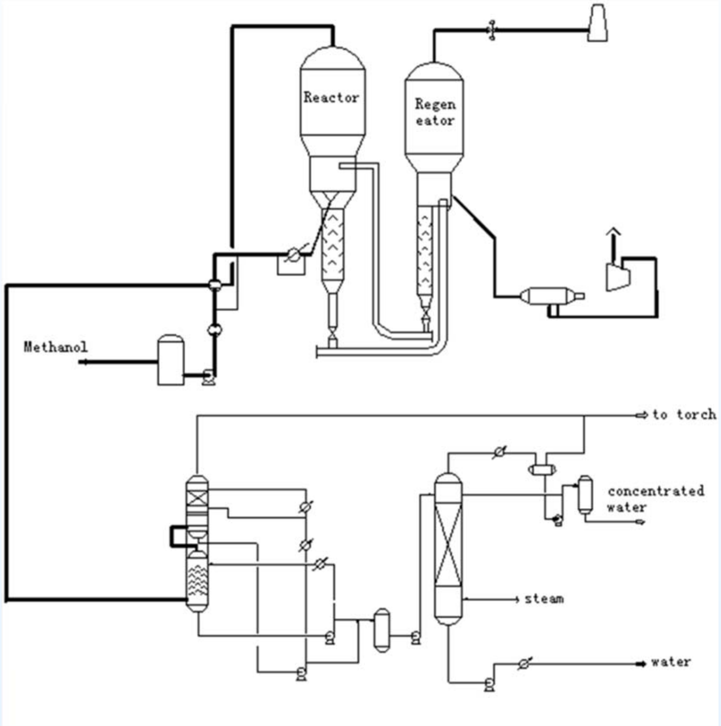
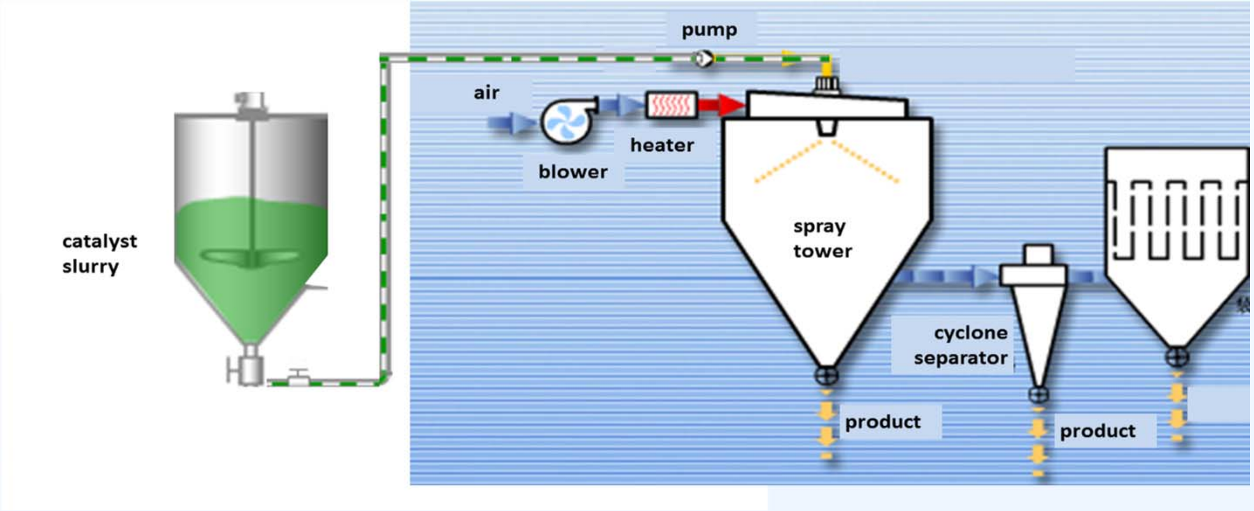
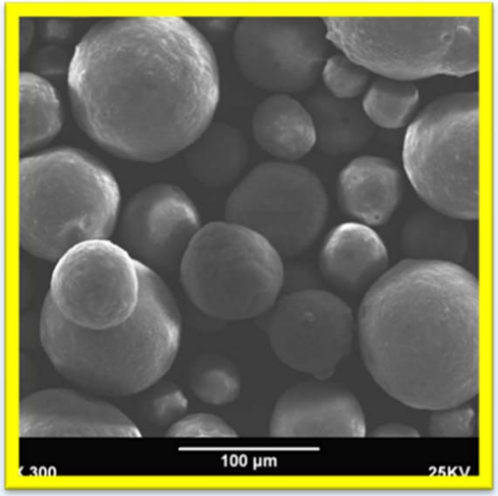


Fig.1 Diagram of MTO process

P. Tian, Y. Wei, M. Ye, Z. Liu, *ACS Catalysis*, 2015

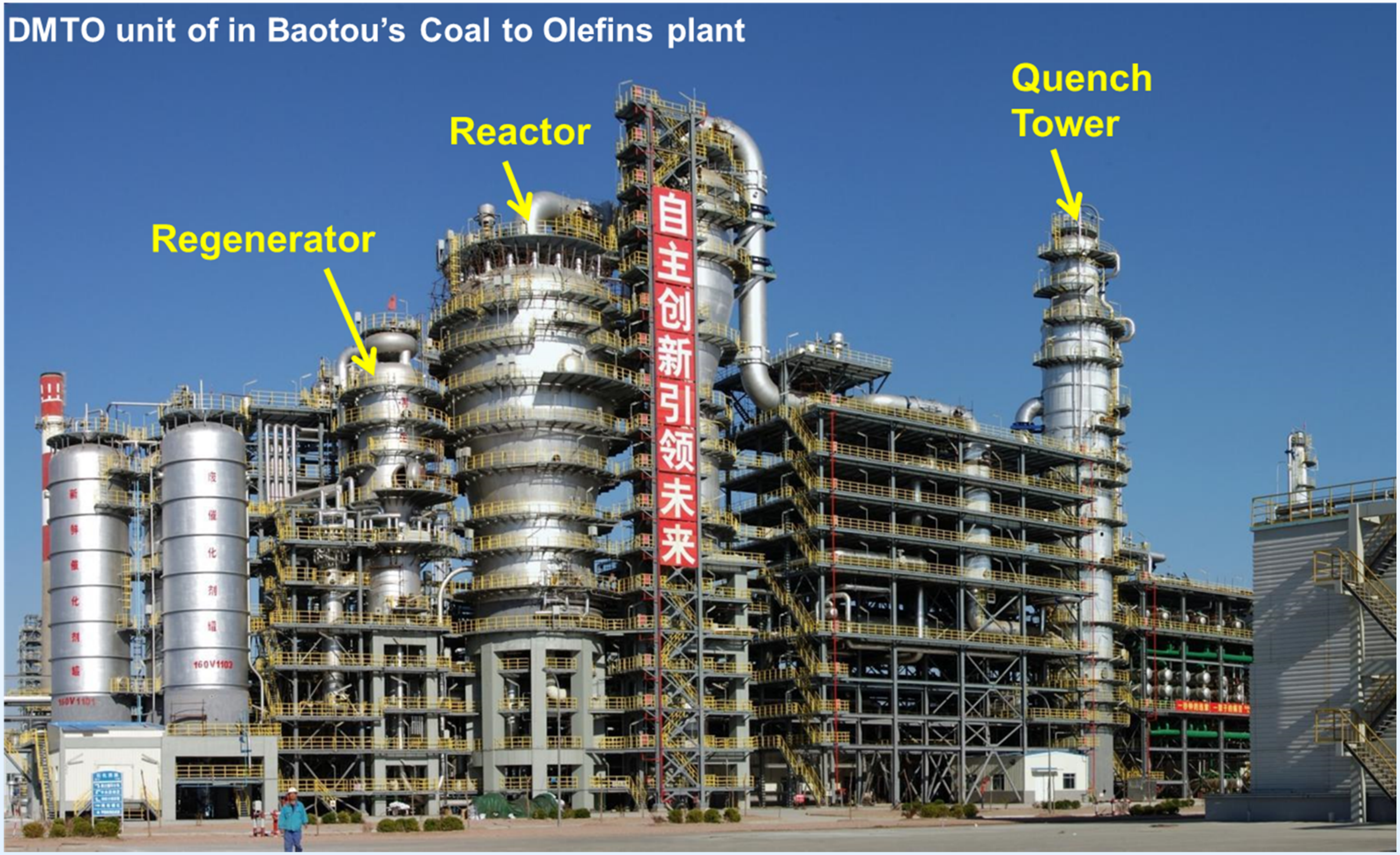
1、Background: MTO catalyst





- MTO catalyst manufacture
  - physical properties close to FCC (fluid catalytic cracking) catalyst:
    - density
    - particle size distribution
    - attrition index measured in the laboratory

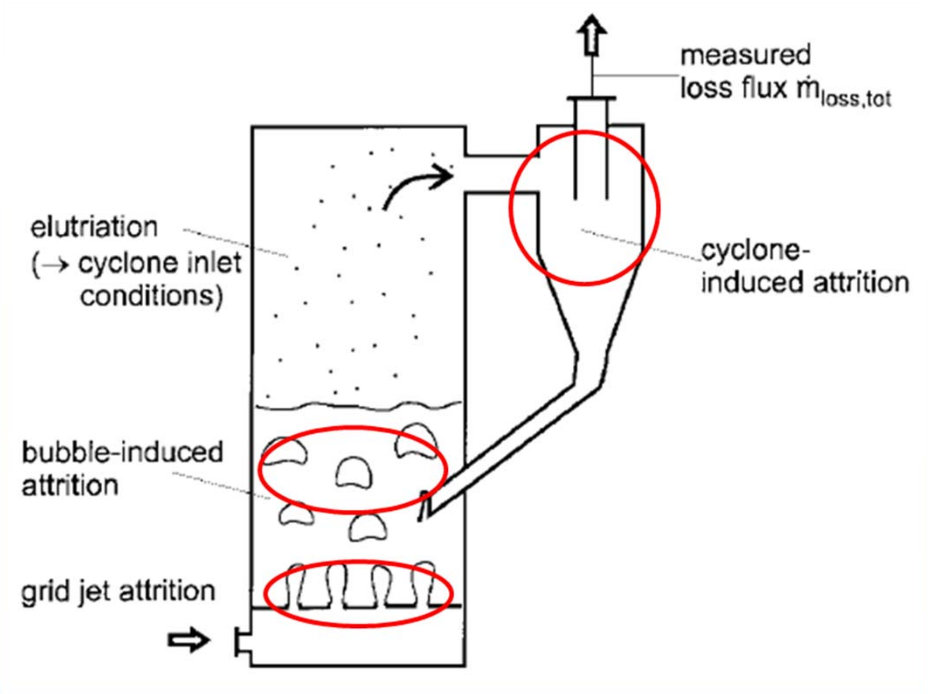
1、Background: MTO unit



- Catalyst loss rate much lower than that in FCC unit
- Slurry of fines at the bottom of quench tower

1、Background: purpose of this study

- Understand the attrition of MTO catalyst at high temperature
  - Comparison of attrition test methods: high velocity gas jets (ASTM-D5757-11) vs Jet cup
  - Influence of temperature, gas velocity, test time on MTO attrition index



J. Werther, J.Reppenhagen. *AIChE Journal*, 1999
C.R. Bemrose, J. Bridgwater. *Powder Technol.*, 1987

2、Experimental: setup

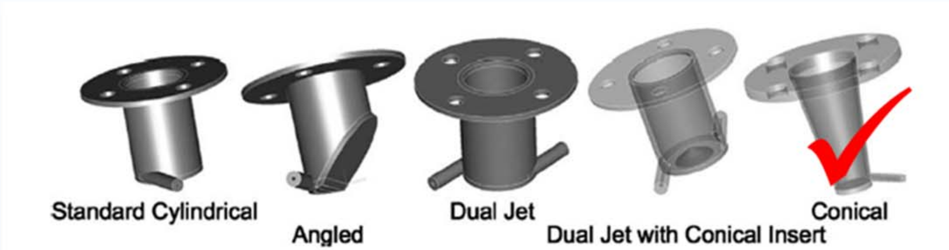
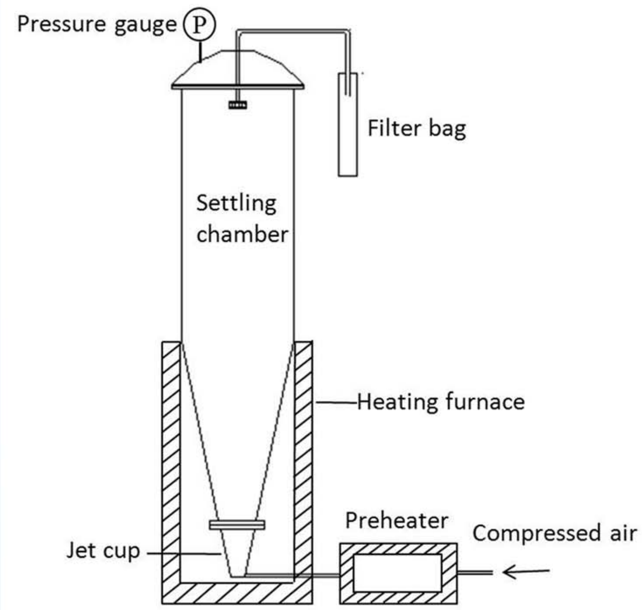


Fig. 5. Five configurations used for evaluating jet cup attrition.

Conical jet cup

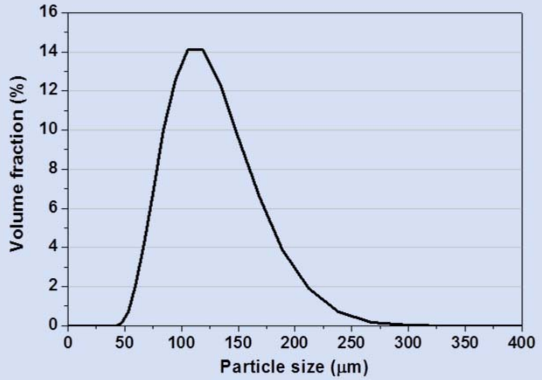
R. Cocco et al. *Powder Technol.*, 2010.



Tab. 1 Properties of sieved catalyst samples

Property	value
Bulk density, g/cm^3	0.75
d_{p50}, μm	111.7
d_{p32}, μm	106.9

Fig. 2. PSDs of samples.



2、Experimental: conditions

No.	Inlet gas velocity, m/s	Temperature, ^{o}C	Time, min
1	88	20	180
2	114	20	180
3	139	20	180
4	158	20	180
5	88	100	180
6	114	100	180
7	139	100	180
8	158	100	180
9	139	20	180
10	139	100	180
11	139	200	180
12	139	300	180
13	139	400	180
14	139	500	180

2、Experimental: methods

- Attrition index (*AI*): the weight percent of particles less than 20 μm or 44 μm (AI_{20} and AI_{44}) after experiments

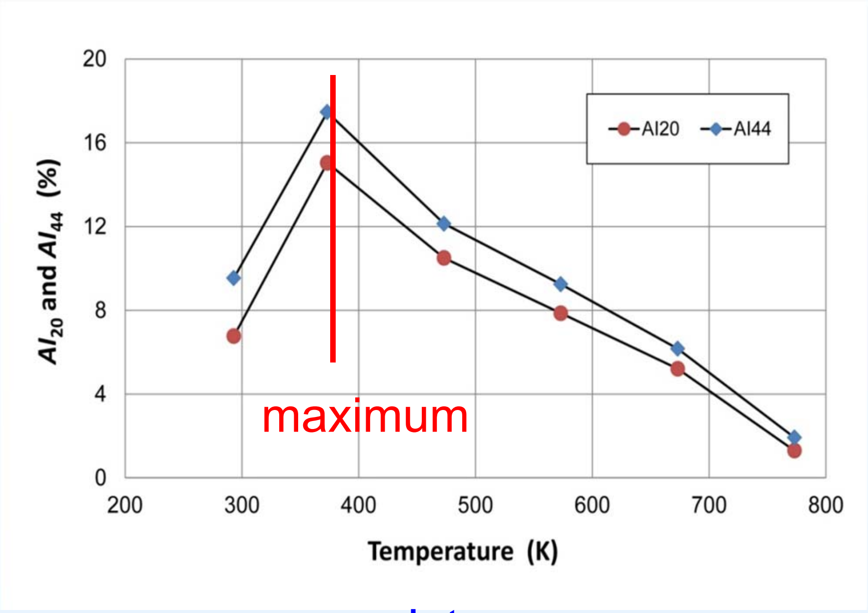
- A material balance analysis showed that the fine loss was less than 1.5% of the initial sample for all individual test

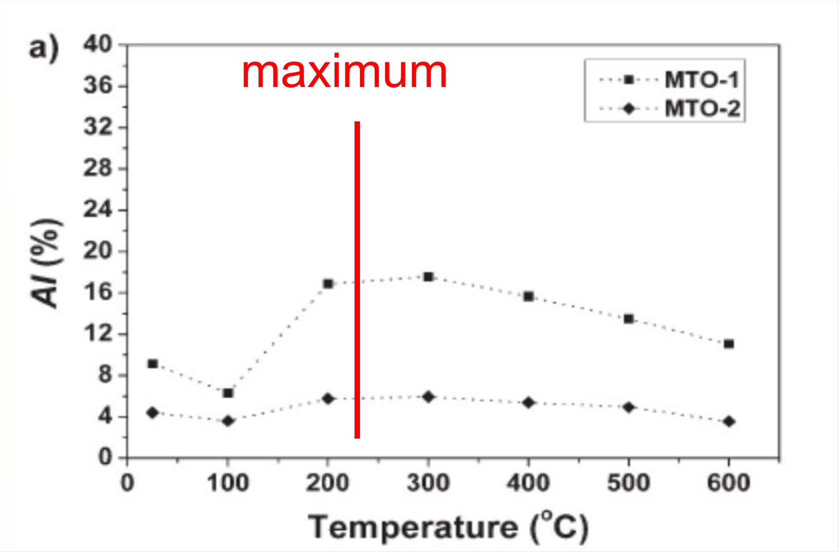
- Particle size distribution (PSD): Malvern laser particle size analyzer (Mastersizer 3000)

- Particles' morphology: Scanning electron microscope (SEM, Hitachi TM 3000)

3. Results: effect of operating temperature

Attrition index (after three hours) with temperature
(inlet gas velocity 139 m/s for jet up and 424 m/s for high velocity gas jets)



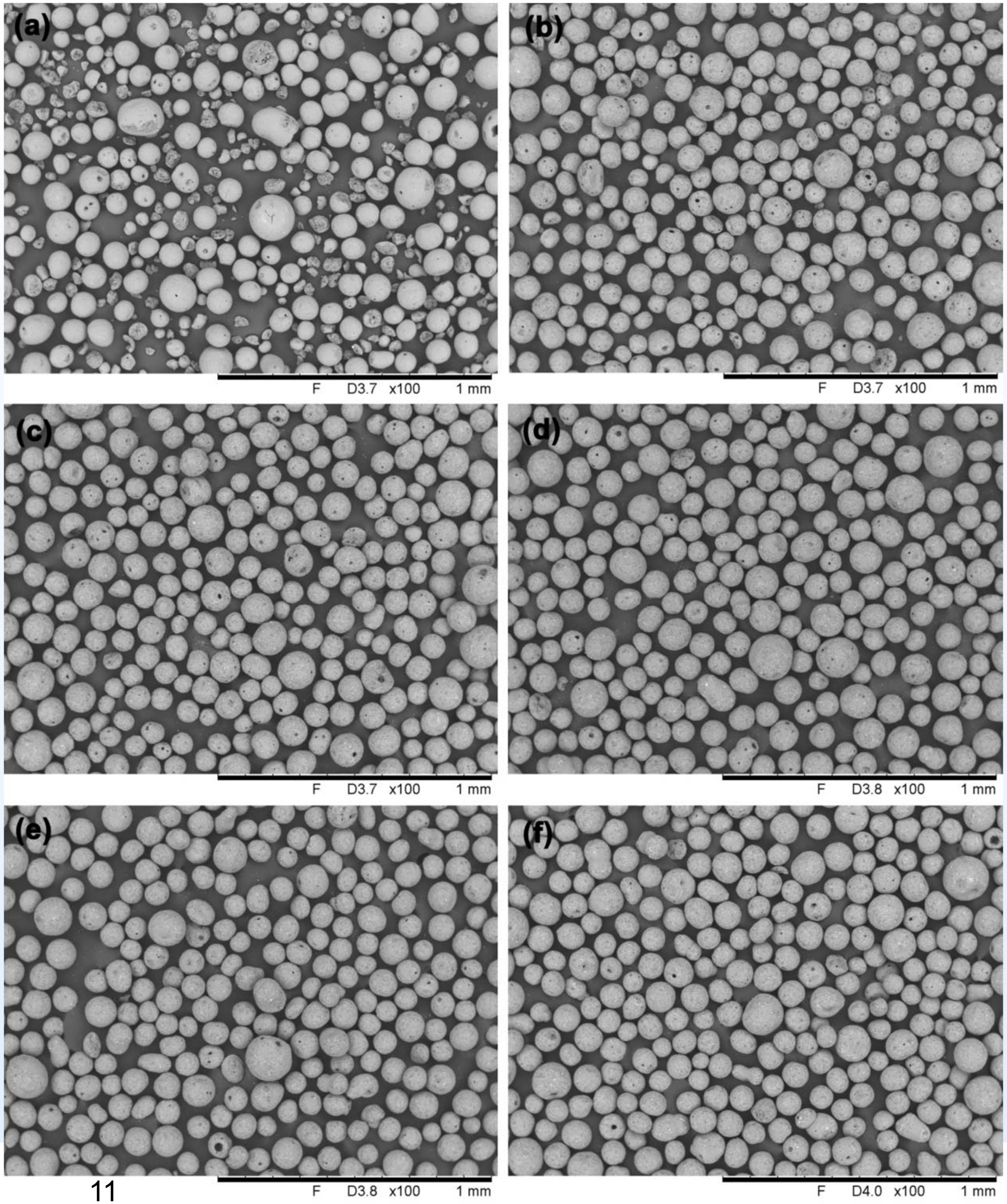


Jet up

high velocity gas jets

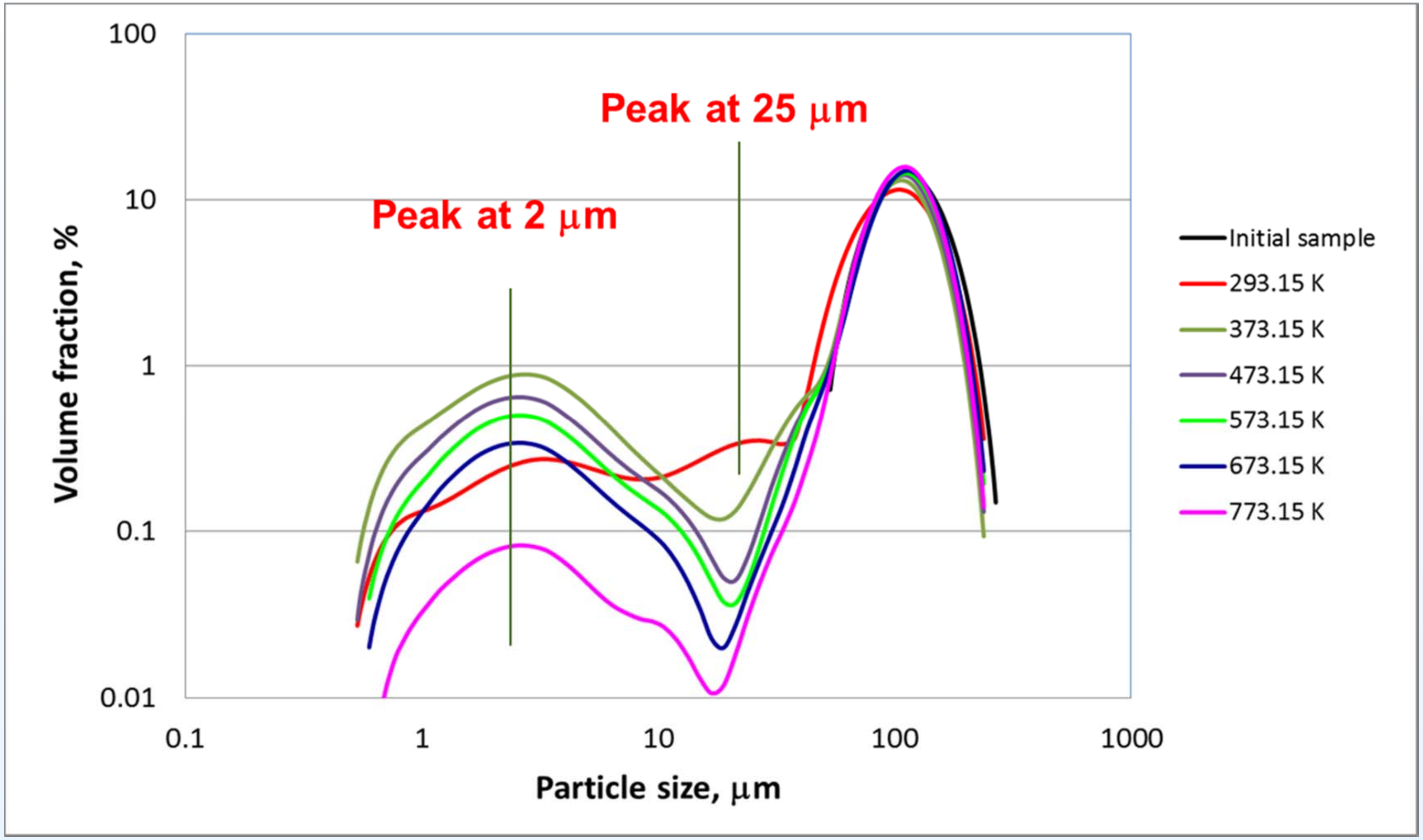
- Attrition index is maximum at 100 °C;
- Attrition at 25 °C may be different from that at high temperature
- Results agree with our previous findings at high gas velocity gas jets

J. Hao, Y. Zhao, M. Ye, Z. Liu, *Chem. Eng. Technol.*, *2016*



SEM pictures of the remaining particles in jet cup after tests: (a) room temperature, (b) 100 ^oC, (c) 200 ^oC, (d) 300 ^oC, (e) 400 ^oC, (f) 500 ^oC.

At room temperature, both *fragmentation and abrasion* exist; only *abrasion* at high temperature.



PSD of the samples after tests at different temperatures.

- Attrition mechanism at room temperature and high temperature (above 100°C) is different for MTO catalyst
  - ✓ At room temperature, both *fragments of 25 μm* and *fines of 2 μm* appear;
  - ✓ At high temperature there are mainly fines of **2 μm**

3. Results: effect of attrition time

Gwyn formulation

$$\boxed{AI = k_1 t^n \qquad (1)}$$

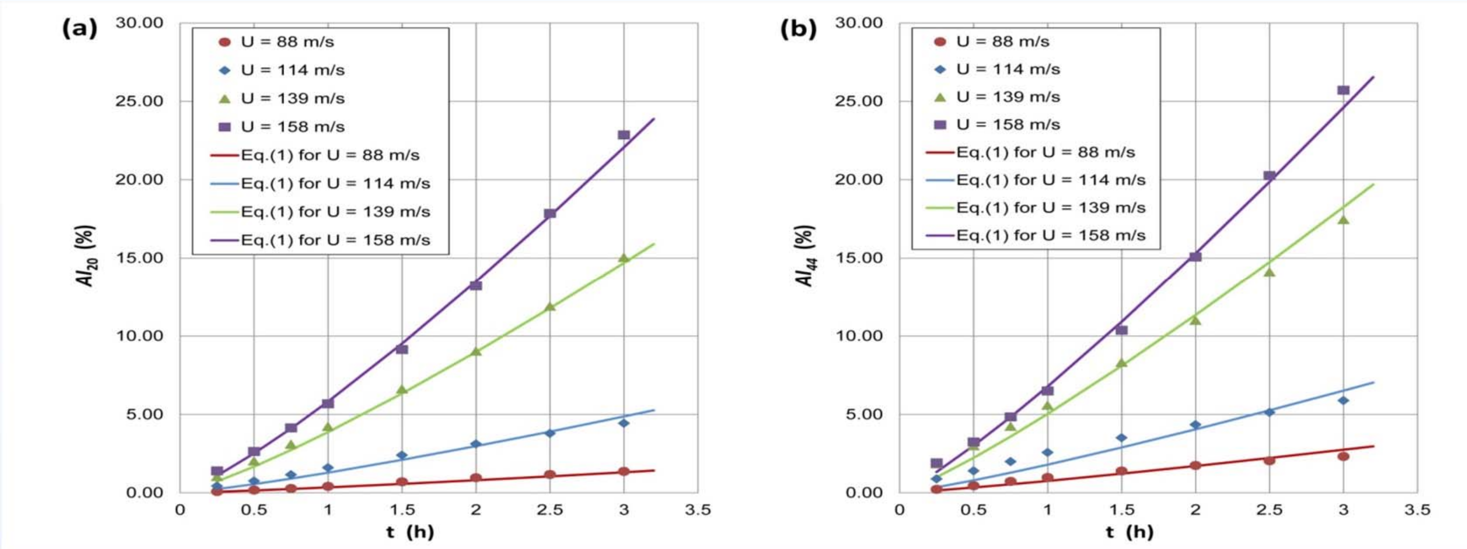
- k_1: attrition rate constant
  depends on operating conditions.
- n: fitting parameter
  depends on the attrition mode and material property.
- t: test time

In our previous experiments in air jets (ASTM-), n was found to be 1.233 for AI_{20} at room temperature (25^{o}C), and 1.236 for AI_{20} at 500 ^{o}C.

J.E. Gwyn. *AIChE J.*, 1969
J. Hao, Y. Zhao, M Ye, Z. Liu, *Adv. Powder Technol.*, 2015

3. Results: effect of attrition time

- Attrition index varies with test time at different inlet gas velocities.



AI_{20} AI_{44}

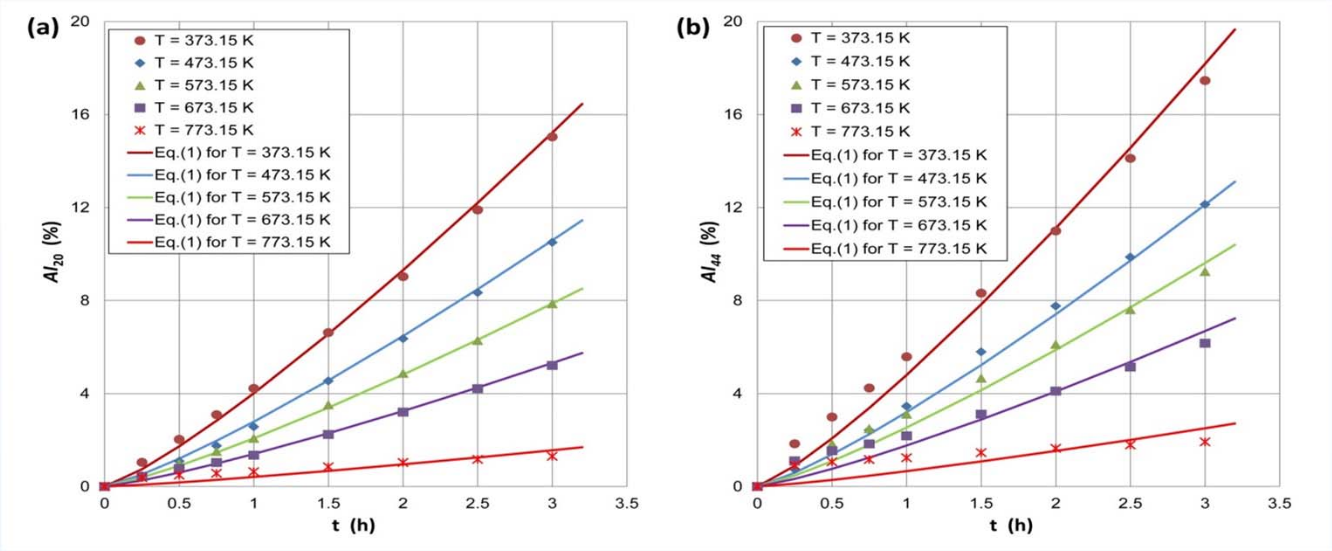
Table 3. k_1 and n for different inlet gas velocities.

Inlet gas velocity, m/s	AI_{20} k_1, h^{-1}	AI_{20} n	AI_{44} k_1, h^{-1}	AI_{44} n
88	0.345	**1.213**	0.758	**1.173**
114	1.284	**1.213**	1.796	**1.173**
139	3.876	**1.213**	5.033	**1.173**
158	5.823	**1.213**	6.784	**1.173**

*: Temperature is 373.15 K.

3. Results: effect of attrition time

- Attrition index varies with test time at different temperatures.



AI_{20} AI_{44}

Table 4. k_1 and n for different temperatures.

Temperature,	AI_{20}		AI_{44}	
K	k_1, h^{-1}	n	k_1, h^{-1}	n
373.15	4.014	**1.213**	4.795	**1.173**
473.15	2.792	**1.213**	3.198	**1.173**
573.15	2.076	**1.213**	2.536	**1.173**
673.15	1.401	**1.213**	1.764	**1.173**
773.15	0.417	**1.213**	0.661	**1.173**

*: Inlet gas velocity is139 m/s.

3. Results: effect of attrition time

- Comparison with previous results in high velocity gas jets
  - Parameter *n*:
    - ✓ high velocity gas jets: *n=1.233*
    - ✓ jet cup: *n=1.213*

      AI_{20}
  - Test time *t*: *the time to achieve steady attrition*
    - ✓ High velocity gas jets: *2 hours*
    - ✓ Jet cup: *15 minutes*

- For MTO catalyst the attrition measured by two methods is quantitatively comparable.
- Test time required in jet cup significantly shorter than that in high velocity gas jets

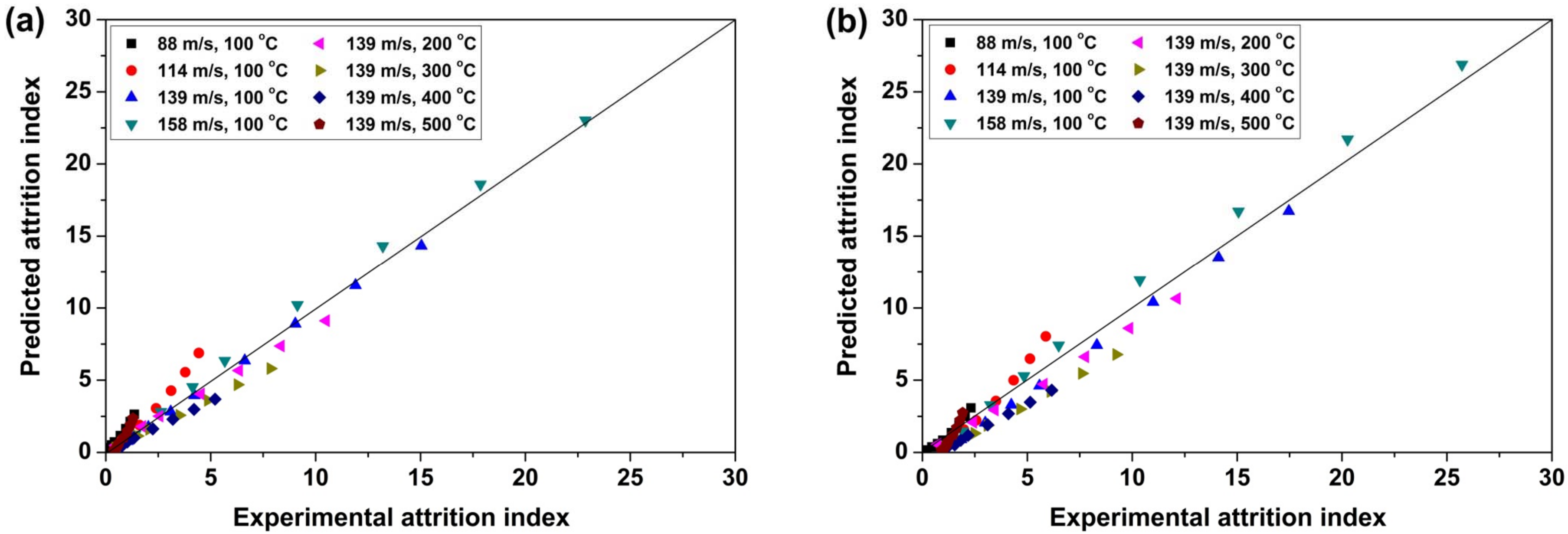
J. Hao, Y. Zhao, M Ye, Z. Liu, *Adv. Powder Technol.*, 2015

3. Results:. Influence of operation conditions in jet cup

A correlation with following formulation is derived:

$$\boxed{AI = k_0 e^{-k_3(T-373.15)} U^m t^n}$$

Parameters	AI_{20}	AI_{44}
k_0	4.65×10^{-8}	5.43×10^{-8}
k_3	0.00452	0.00452
m	3.7	3.7
n	1.213	1.173
R^2	0.986	0.958



Comparison between the experimental results and the predicted *AI*: (a) AI_{20}, (b) AI_{44}.

4. Conclusions

- Attrition mechanism of MTO catalyst is different for room temperature and high temperature (above 100°C)
  - both fragmentation and abrasion exist at room temperature
  - abrasion is dominant at high temperature
  - attrition test results at room temperature cannot be directly used for high temperature
  - fines from abrasion at high temperature are around *2 μm, which is hard to be captured by cyclones.*
- For MTO catalyst quantitatively comparable results can be obtained in both high velocity gas jets and jet cup method; but jet cup method needs significantly shorter test time
- A correlation of MTO catalyst attrition in high temperature jet cup with operation conditions fits the experimental data very well

Thank you

for your attention!

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