Structural Properties of Nanoparticle Emitted from DI Diesel Engine

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Introduction

Recently a hazard of nanoparticle effect on human health has been paid attention among a lot of researchers. Therefore, there is a movement to make worldwide regulation of particle emitted from automotives. A target particle emission of Inter-laboratory correlation exercise of GRPE/PMP research council of the United Nation is only a solid particle. One of the reasons is that solid particle has longer lifetime and much possibility to reach human body compared to liquid particle.

To estimate the stability of diesel nanoparticle is essential to make suitable regulation, and degrees of graphitization of these particles have much influence on their stabilities. Therefore in this study, the degrees of graphitization of particles emitted from diesel engine, as a function of particle mean diameter have been measured using ELPI and Raman spectroscopy.

Experimental

4 cylinder 4000cc common rail DI diesel engine was applied and its exhaust before DPF was sampled. The sampled gas was diluted by a hot air (150degree) to avoid an effect of volatile particle and then introduced to ELPI (Decati) to sort by particle mean diameter (12 stages, 14 to 1233nm). Raman spectroscopy measurements of these collected samples were carried out using NRS-2000 (Nihon Bunko).

2 peaks of Raman sift peculiar to soot measurements were observed. One is near 1590cm^{-1} (G band) corresponding to 6 membered ring structure and another is near 1350cm^{-1} (D band) corresponding to dangling bond. Therefore, a ratio of intensity of D band and G band indicates the degree of graphitization. In latter section, a degree of graphitization as a function of particle mean diameter will be discussed using the ratio of intensity of D band and G band (D/G).

Results and discussion

From the results of Raman spectroscopy measurement of diesel particle, it is observed that the smallest particle (about 14nm) has the largest D/G and the value become smaller with larger particle. This indicates that the degree of graphitization progresses in particle growing up process from smaller to larger. And graphitization progresses even in fractal agglomeration stage (over 50nm). The D/G of smaller particle is almost same with that of carbon black and this indicates that a small particle has almost same structure with amorphous carbon. On the other hand, larger particle have almost same D/G with a graphite carbon material, nevertheless, the particle emitted from engine has broader peak of G band than the graphite carbon material. It is supposed that a larger diesel particle is highly graphitized as well as a fine carbon nevertheless crystalline continuity revel is low.

In case of enhancing engine load, the D/G ratio becomes to fall off at smaller mean diameter. This is because, maximum incylinder temperature is increased with increasing engine load, and this accelerates graphitization compared to physical growth of particle. Same feature was observed in case reducing engine revolution speed. It is because reducing engine speed causes longer residence time at high temperature. Therefore, longer residence time also accelerates graphitization.

The D/G value is increased by passing through DPF in all mean diameters. It is supposed that a crystalline structure is destroyed in oxidation process at DPF.

Conclusion

The degree of graphitization was obtained as a function of particle mean diameter with ELPI and Raman spectroscopy.

Smaller particles have almost same D/G with carbon black. Graphitization proceeds with larger particle, even in fractal agglomeration stage. The D/G intensity ratios of larger particles are almost same with fine carbon, but widths of peaks are different.

Graphitization progresses in smaller particle with higher engine load because of higher maximum temperature. Graphitization also becomes to progress in smaller particle by lowering the engine speed because of longer residence time at high temperature.

The degree of graphitization is decreased by through DPF by re-burning process..

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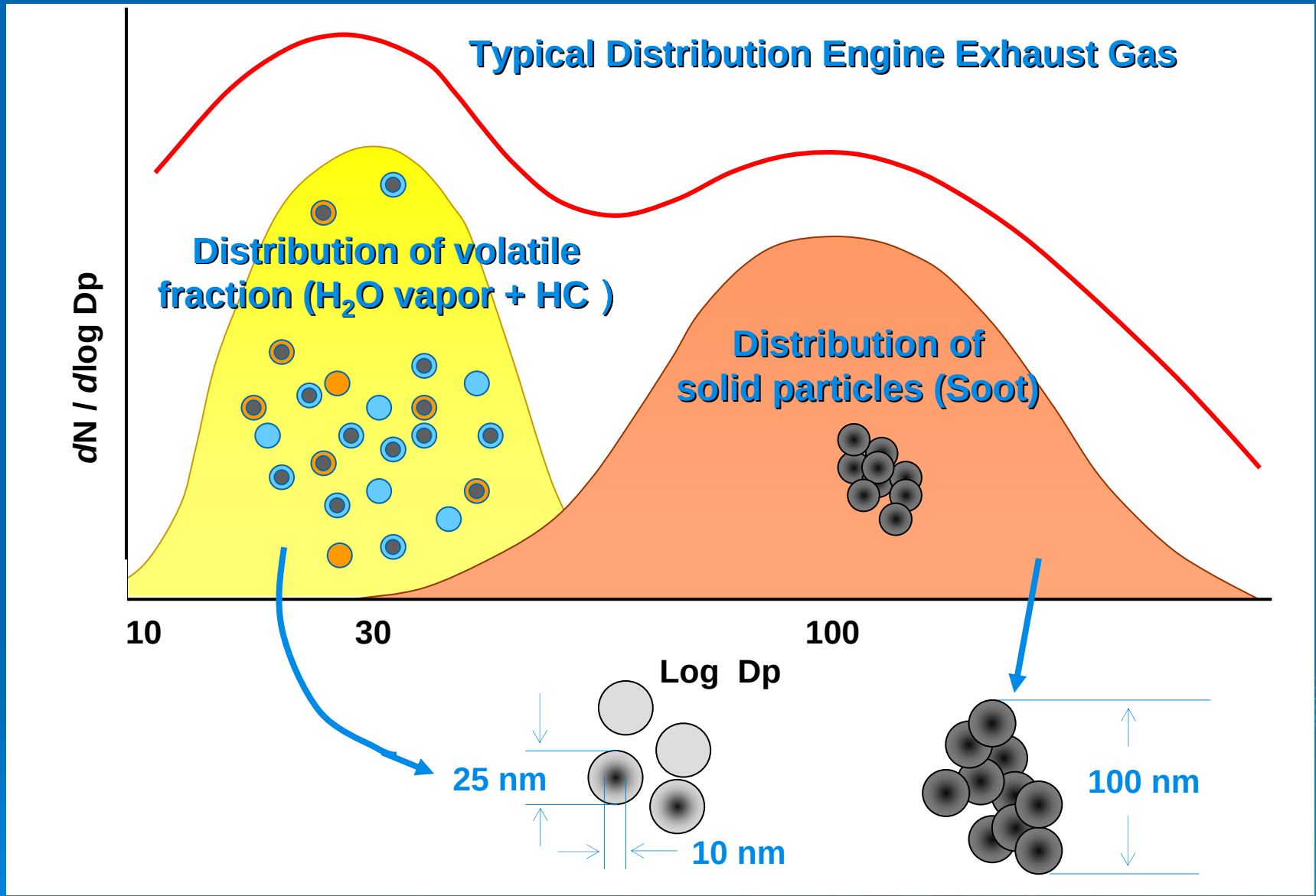
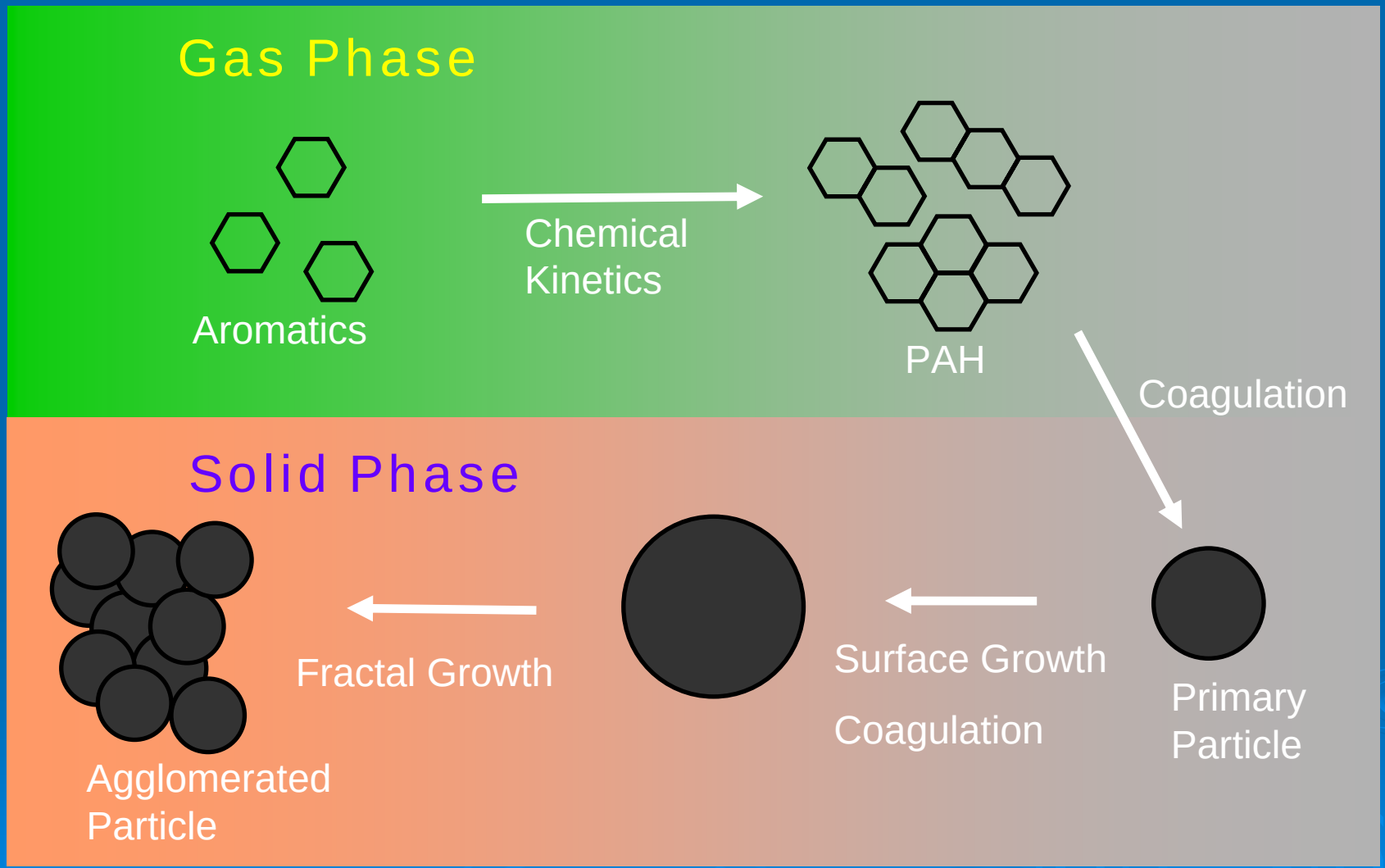
Typical Particles in Diesel Emission

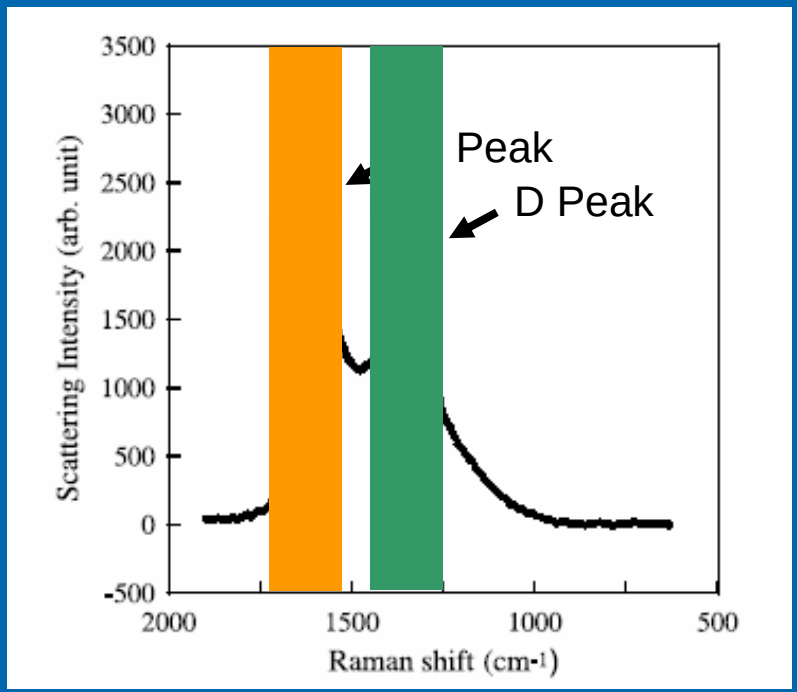


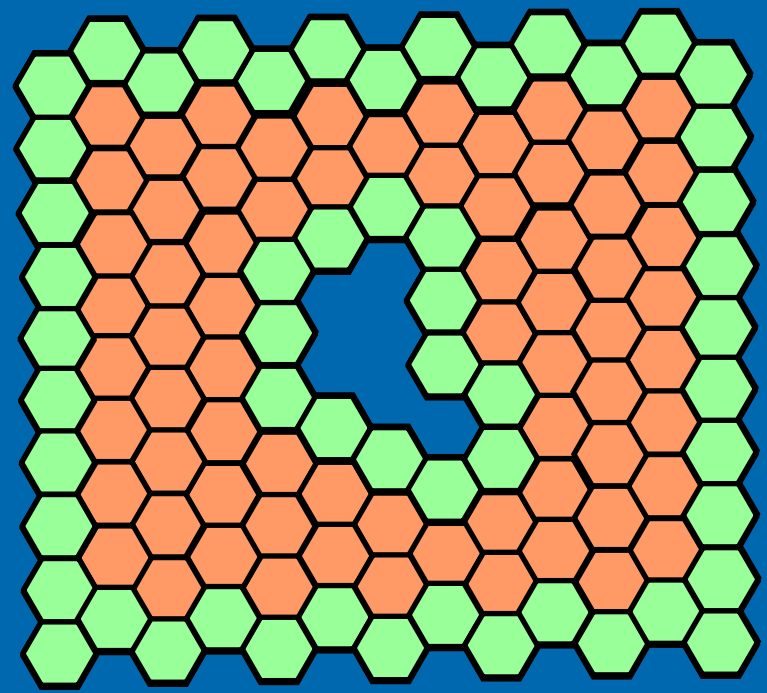
Growing Process During Combustion



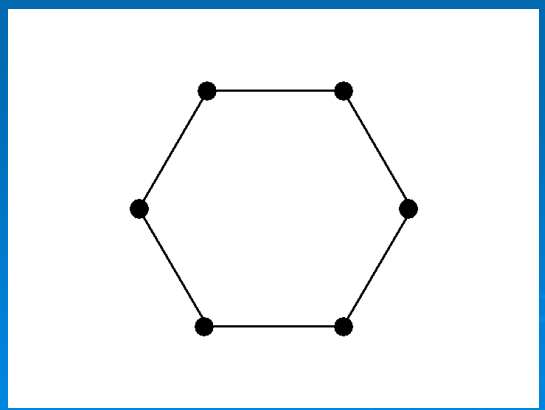
Frenklach, M., Pys. Chem. Cem. Phys., 2002

Microstructure of Particles

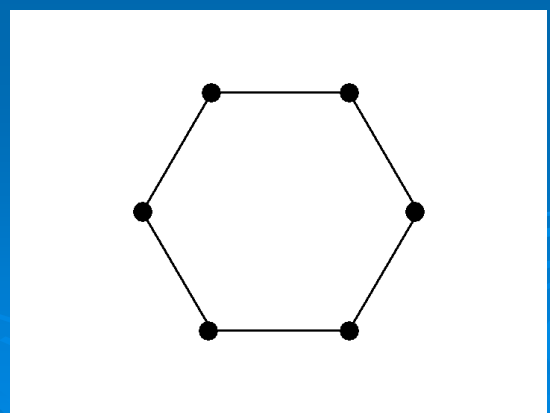




Zhu, J., et al., Proc. Combust. Inst., 2004



G band



D band

Objectives

Small particles with solid core have a possibility to do damage to human health.

To estimate the effects and to regulate, we must know a stability of solid nanoparticles.

Degrees of graphitization affect on lifetimes of particles.

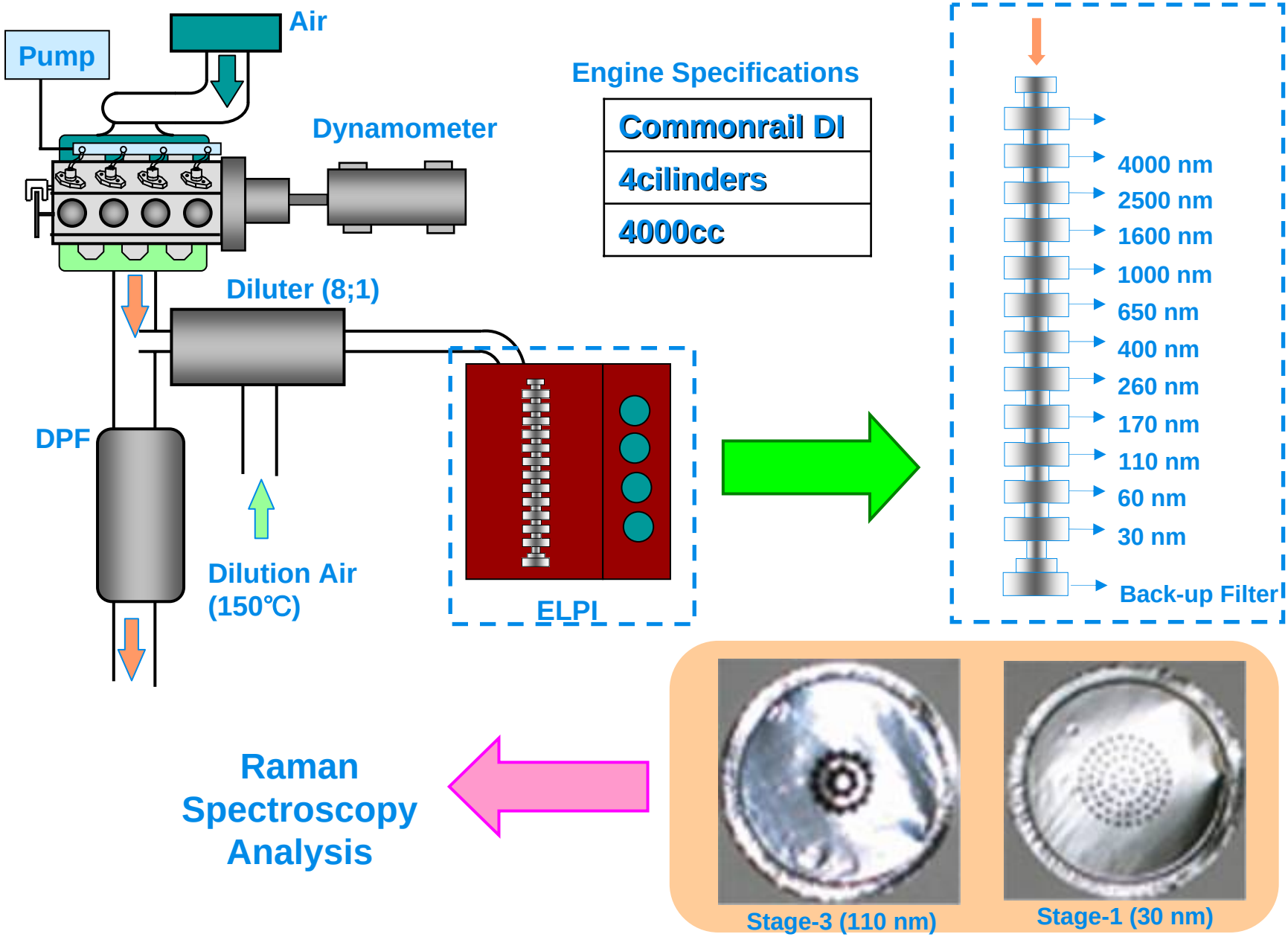
So, in this study, We will discuss…

a degree of graphitization using the ratio of intensity D band / G band as a function of particle mean diameter.

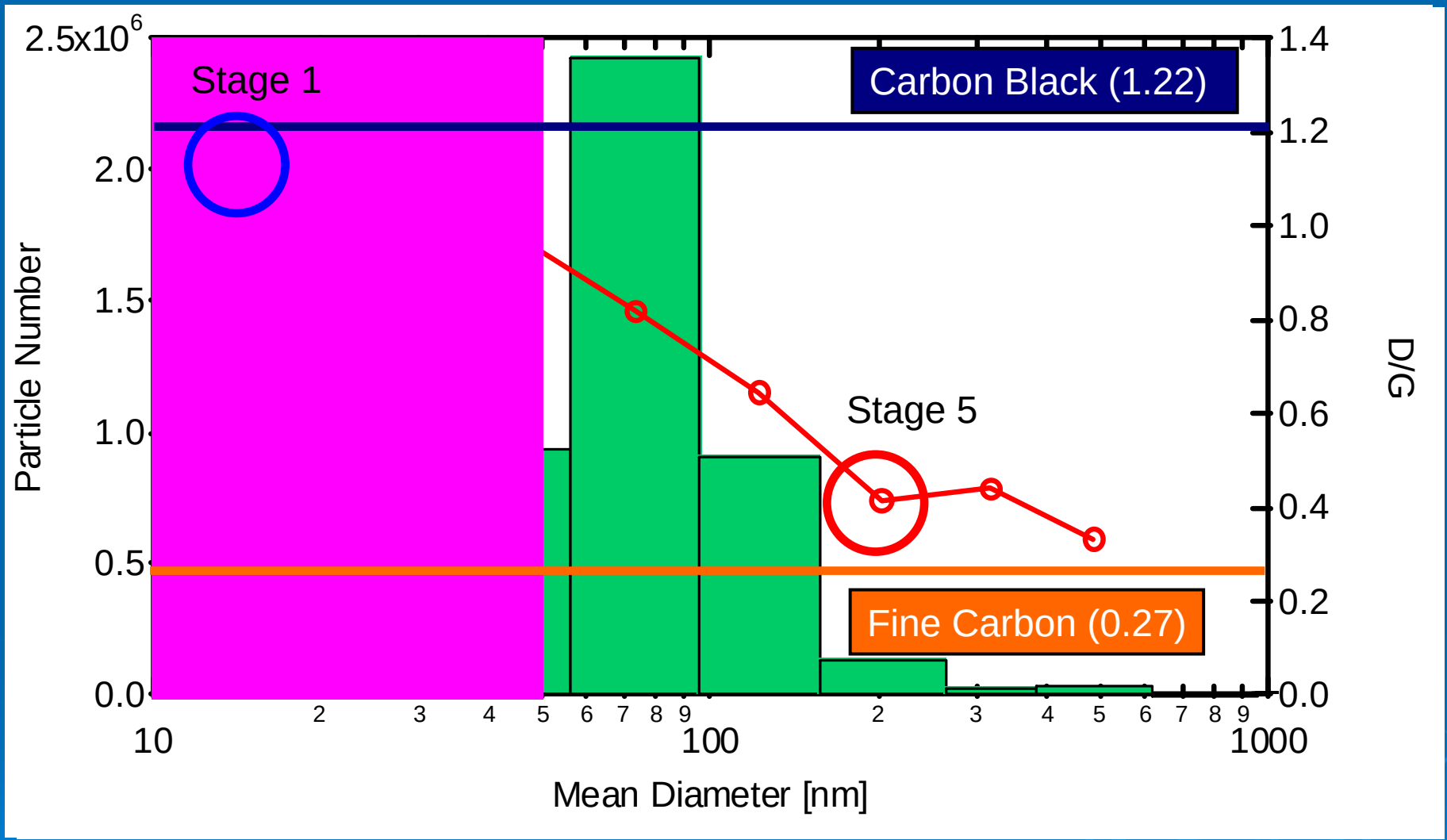
the process of particles graphitization progress, supposing that particles glow up from smaller to bigger.

how the degree of graphitization changes with changing engine condition (engine load, engine speed and DPF).

Experimental Apparatus



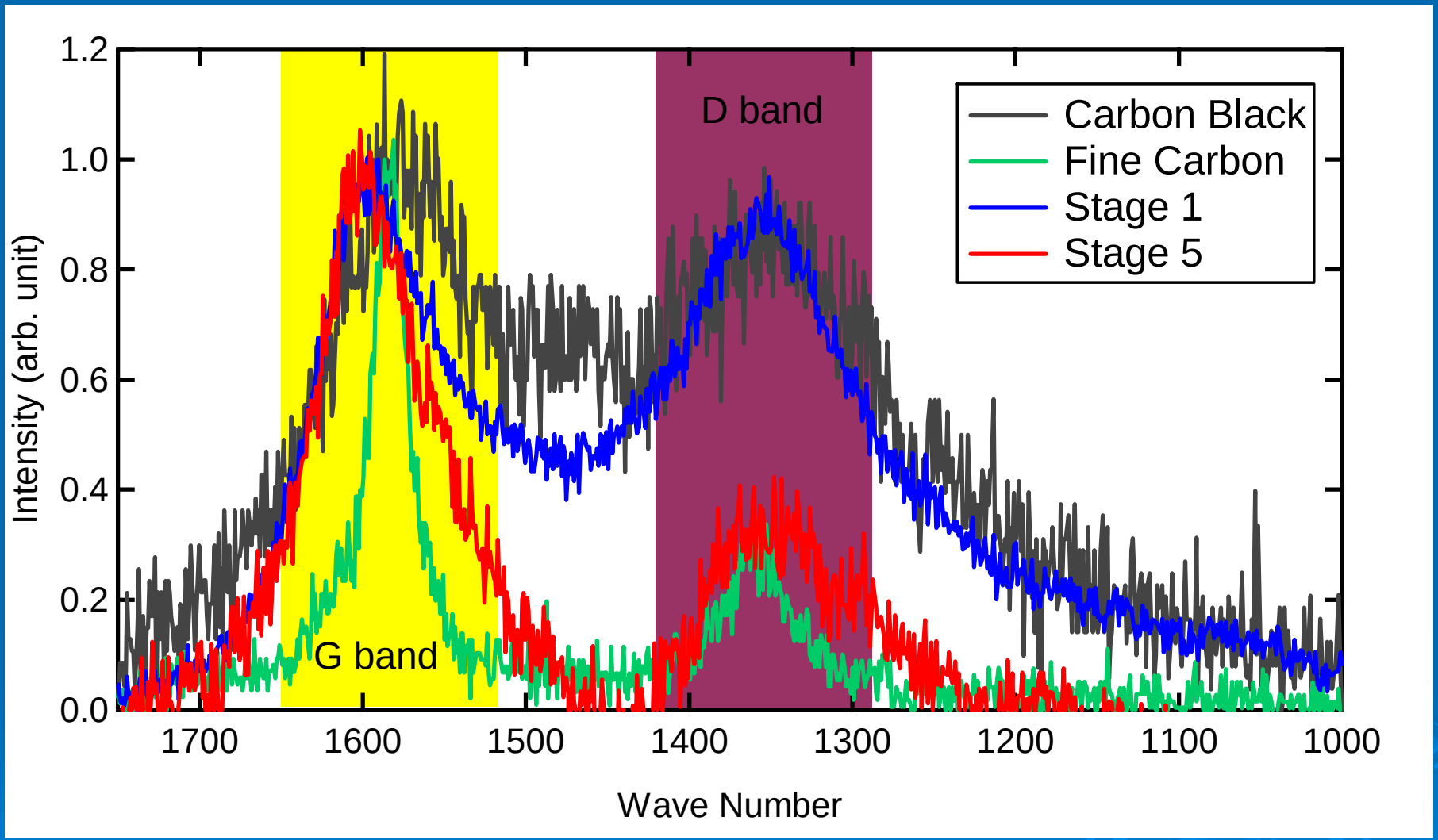
Result (Common Properties)



Graphitization progresses even in fractal agglomeration stage.

Small particles have almost same D/G ratio with Carbon Black, but the values became closer to Fine Carbon as enhancing diameter.

Result (Raman Spectrum)

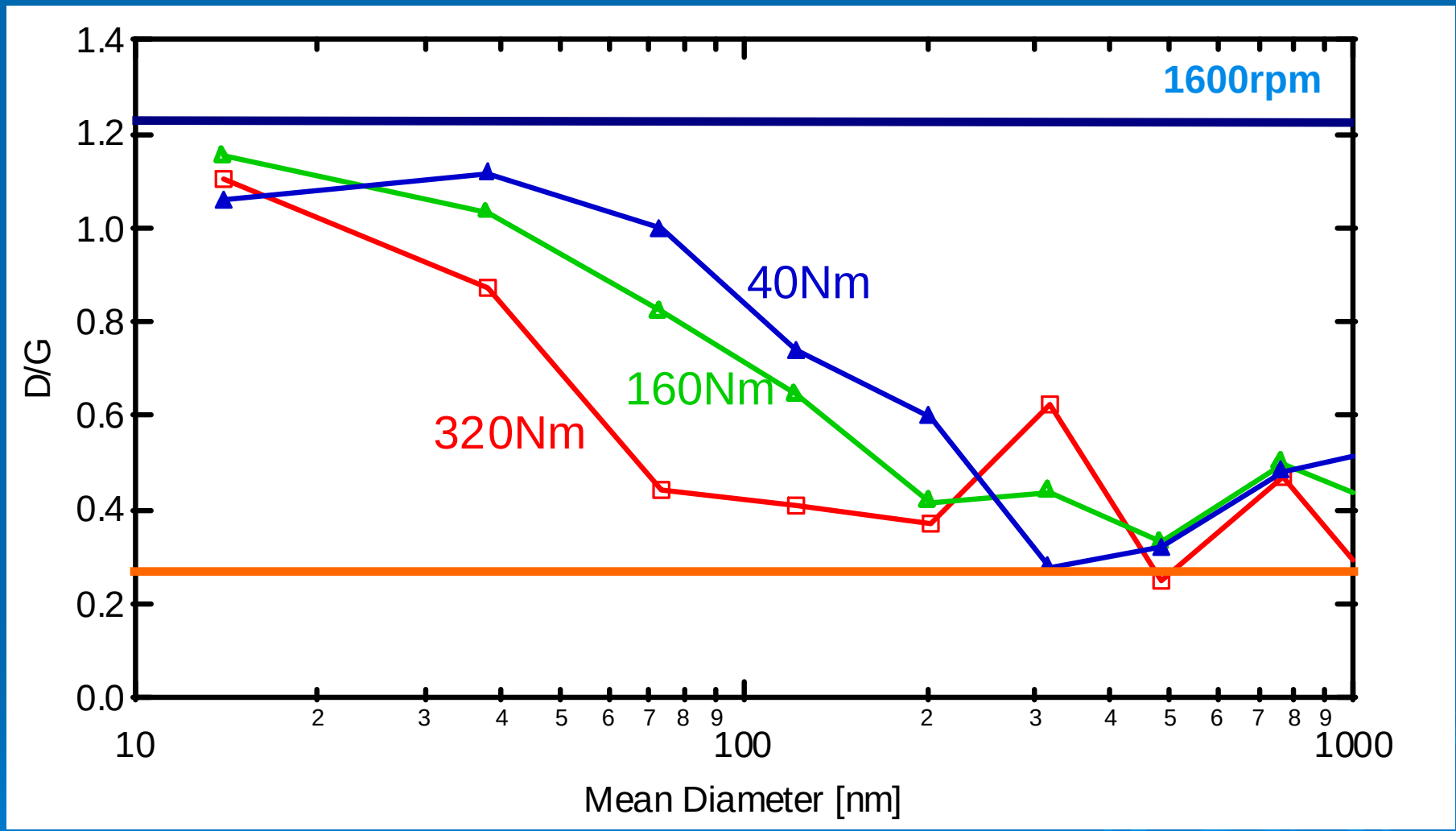


No difference is observed in the G band width, Stage1 and Carbon Black.

The width of Fine Carbon peak is narrower than that of stage5.

→ This will be because of a structural variety of particle from diesel.

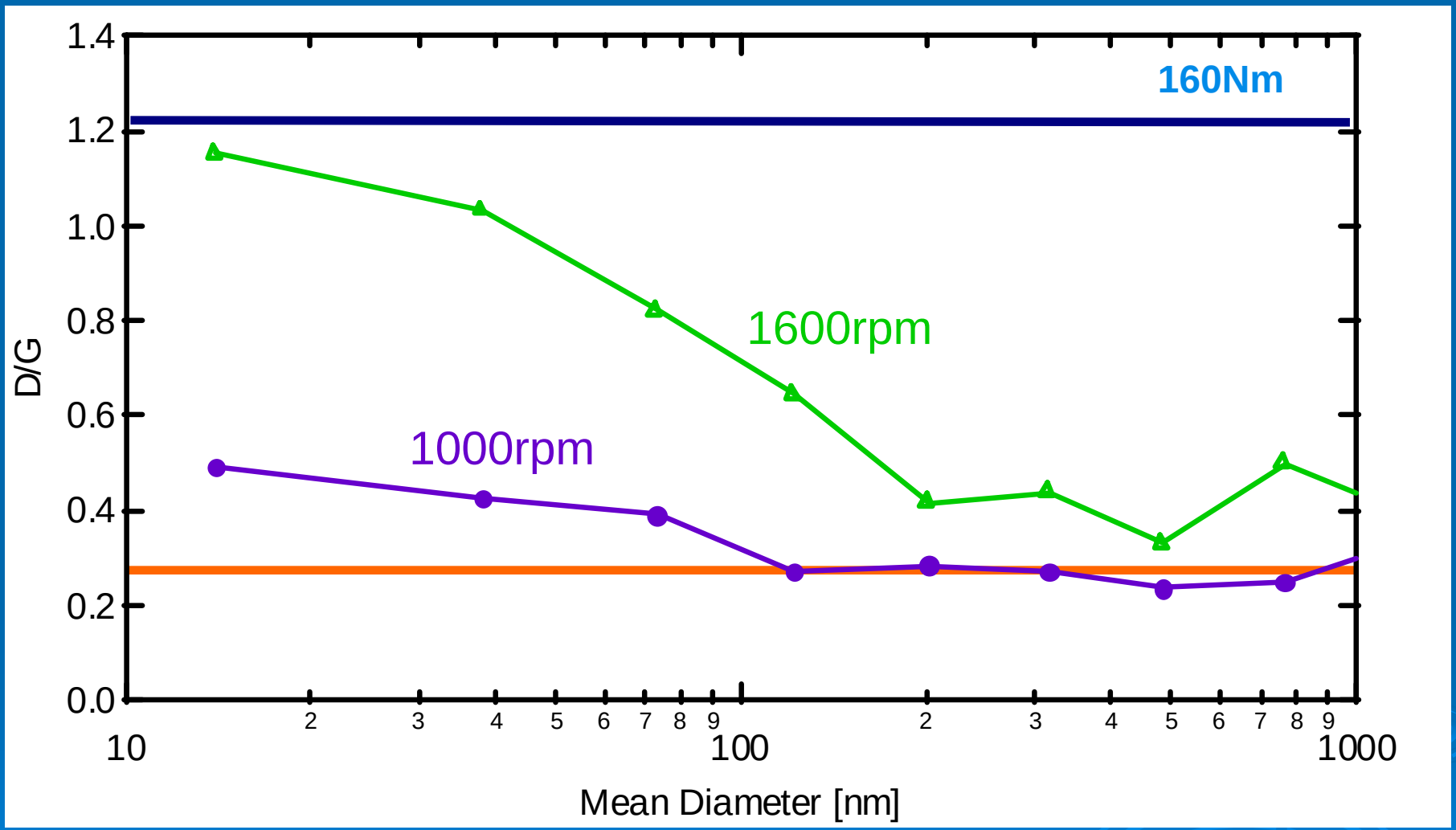
Result (Load Dependence)



Graphitization progresses in smaller particle with higher load condition

→ Higher maximum temperature accelerates graphitization.

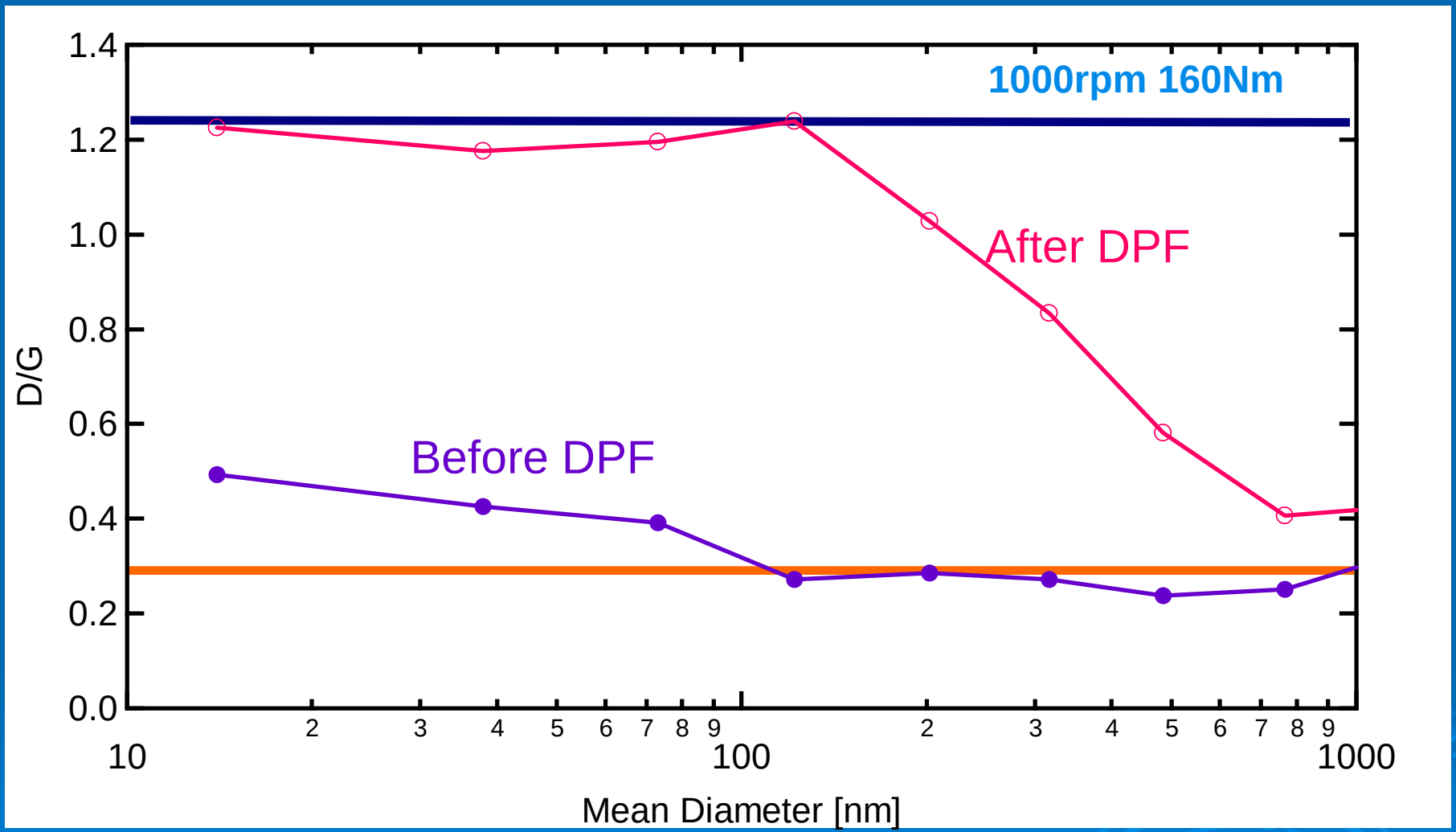
Result (Revolution Dependence)



Graphitization progresses in smaller particle with lower engine speed.

→ Longer residence at high temperature accelerates graphitization.

Result (Before / After DPF)



Particles passed through DPF are almost amorphous

→ Crystalline structure is destroyed in oxidation process at DPF

Conclusions

Raman spectroscopy has been applied for diesel particle classified by ELPI

The degree of graphitization (D/G ratio) were acquired as a function of particle mean diameter.

Smaller particle has almost same D/G with carbon black. Larger particle is more graphitized, and even in fractal agglomeration stage, this feature is observed. The D/G ratio of larger particle is almost same with fine carbon, but widths of peaks are different.

The D/G value become to fall off in smaller particle in case enhancing a engine load because of higher maximum temperature.

Graphitization also progresses in smaller particle by lowering a engine speed because of longer residence time at high temperature.

The Degree of graphitization is decreased by passing DPF.

Particle Effects for Human Health