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Gas-solid reaction induced particle collision and aggregation



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ABSTRACT

Chemical reaction induced particle collision and aggregations in gas-solid phase reaction were presented in this work. The characteristics of particle collision and aggregations in non-catalytic gas-solid phase reaction- petcoke particles combustion process in air was experimentally analyzed. The reason for the formation of different aggregation structures is the reactant concentration distribution and particle position. Different spatial positions of solid particles caused the non-uniform concentration distribution of gaseous reactant and product around particle surface. The non-uniform distribution of gaseous reactant results in cohesive force, which lead to particle collision and aggregations. The aggregates of multi-particles tend to show "I" and "L" structure with the effect of cohesive force and drag force. Simulation work also were conducted to analyze the reactant and product concentrations, release velocity of product and bearing force of solid particles. The mechanisms of different particle aggregation patterns were demonstrated.

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1. Introduction

Particle aggregation is a common yet critical phenomenon that presents in many applications. The particle aggregation was deeply investigated to understand the flow dynamics and applied to industry [1–3]. For example, Particle aggregation decreased the emission of fine particles, which resulted to the air pollution (*e.g.* PM 2.5) [4]. The self-assembly of nanoparticles also is a kind of aggregation to control the quality the nanomaterials [5–7]. The previous work proposed various principles to forecast the aggregation of particles in gas-solid reactions. However, limited studies introduced the effect of chemical reaction on micro particles aggregation. Factors affecting particles aggregation (Van der Waals forces, electrostatic force, capillary force, magnetic force, drag force, and so on) differed with particle size and properties. Hence, we mainly introduced the progress of aggregation mechanisms in respect to different particle size.

Gas-solid fluidized beds and entrained flow beds are widely used in chemical engineering process. Particle aggregation is a general phenomenon, which was widely investigated using cold state and simulation methods [8–10]. The particle size in fluidized bed and entrained flow reactors ranged from centimeters to micrometers. Factors that affecting particle aggregation also were com-

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plex. Moisture content of solid particles flows is essential to the aggregation efficiency because of the liquid-bridge force and hydrogen bond. The aggregation efficiency generally increased with the moisture level of the gas-solid flows [11]. The operating conditions, which affect drag force and flow conditions, also significantly affect the aggregation of solid particles in reactors. Relevant work by Zhou et al. [12,13] showed that higher gas velocity and fluid density and lower particle cohesion and collision between agglomerates decreased the agglomerate size. The aggregation characteristics in fluidized bed reactors were different due to the various lowest mixture kinetic energy in middle and bottom regions [14]. Collision frequency and aggregation efficiency in fluidization process directly affects the aggregation. In general, the aggregation efficiency increased with the collision frequency when the impact speed is lower than the critical aggregation speed [15,16]. Zhu et al. [17] found that the aggregation efficiency increased with the decrease of particle size and density. The effect of particle size and density are more important in aggregation process compared with particle sphericity. Solid bridge force also affects the aggregation process when chemical reactions changed the surface properties of solid particles [18,19]. These investigations revealed the factors affecting fine particles aggregation, optimized the flow conditions and improved the performance of reactors.

Nanoparticles are widely used for environmental and energyrelated process resulting from its excellent properties. In investigations on nanoparticle aggregation, the aims of these studies are mainly to understand the aggregation mechanism [20,21], monitor

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Table 1

Proximate and ultimate analysis of sample.

Proximate analysis (Air dried basis, wt.%)	Moisture	Volatile Matter	Ash	Fixed Carbon
Ultimate analysis (Air dried basis, wt.%)	0.71 C 91.63	7.99 H 3.46	2.03 N 1.68	89.27 S 2.78

the aggregation process to control the aggregate quality and minimize aggregation. The cluster scale would influence the function of nanomaterial [22]. High surface energy, capillary forces, hydration forces and chemical bond plays important role in both regimes of the nanoparticle aggregation [23]. Therefore, coating method, secondary particle and dispersing medium methods were adopted to change the surface properties of nanoparticles and prevent its aggregation [23–25]. During the coating process of nanoparticles, it was found that the change of surface characteristics also altered the electrostatic and Van der Waals forces [26]. The size of nanoparticles increased with the inter-particle forces. Sometimes, the aggregation of nanoparticles in reactor need to be restrained to achieve coating on particles individually. It was proposed that mechanical vibration and surface modifying effectively decreased the aggregate size [27]. Andino et al. [28] further found that the bed height in microjet and vibration assisted fluidized bed expanded several times more than that in vibration assisted fluidized bed. In investigations on nanoparticles aggregation, relevant work found the chain formation of fine particle aggregates in 1970 [29]. At the same time, the aggregations of carbon black also were studied during combustion process in previous works [30,31]. Interestingly, the solid particles showed dendritic aggregation in relevant work [29,32-34]. It was also revealed that the fractal structure of carbon black is related to the reaction temperature and reactant [35]. Comparing with reaction-limited aggregation, the diffusionlimited aggregation tend to form dendritic structure [36]. Influences of chemical reactions only were deeply studied in nanoparticles aggregation.

In this paper, we introduced and analyzed a new factor (force induced by chemical reactions) resulting to the micro-scaled particle aggregations in non-catalytic gas-solid phase reaction (combustion reaction). The solid particles used in this study are petcoke particles and the gaseous reactant is air. The combustion reaction experiments of petcoke particles were carried out using a visual *in situ* micro-reactor and combustion of particles also was numerically analyzed in this work. The turbulence induced by gas flows into the reactor chamber was excluded in this non-catalytic gassolid phase reaction. Novel mechanism resulted to particle aggregation in non-catalytic gas-solid phase reactions is revealed in this study.

2. Experimental section

2.1. Samples

The petcoke sample used in this work was dried, crushed and screened to the size range of 100–200 μ m. The proximate and ultimate analysis of petcoke were shown in Table 1. It was found that petcoke is rich in carbon and the ash content in petcoke is very low, which decrease the effect of adherence of melted ash on sapphire pieces.

2.2. Non-catalytic gas-solid phase reaction process

Combustion of solid fuel is a typical non-catalytic gas-solid phase reaction and combustion of petcoke particle swarms was carried out in this work. The combustion process of petcoke were observed using an in-situ high temperature stage (Linkam, UK) coupled with microscope system (Leica, Germany) [37]. The schematic of the high temperature stage is shown in Fig. 1. The whole reaction process can be observed and recorded by the microscope. In this study, petcoke particles were spread on the sapphire slip and placed in the ceramic crucible of the heating stage. The samples were heated to the reaction temperature at the heating rate of 100 °C/min. The heating process was proceeded in an inert environment. Then the gas flow was switched from Ar (99.99% purity) to Air (99.9% purity) at the flow rate of 0.1 L/min to decrease the turbulence. The microscope camera system also began to record the aggregation phenomenon during the reaction process. The recorded video was converted to series of graphs to be further analyzed. The time interval can reach 0.2 s between series converted photos. The combustion experiments of petcoke particle were repeated for more than 20 times to count the aggregation frequency.

2.3. Simulation work

To simulate the combustion process in this experiments, the reaction conditions are similar to the experimental reaction conditions. We selected the species transport model in FLUENT to calculate the reaction process and analyze the pressure on particles. The combustion reaction of the fixed solid particles was in a closed space and the outlet condition is the pressure outlet. The SIMPLE method was applied for pressure coupling. The combustion reaction on particle surface is based on energy equation and species transport equation coupling. The release velocity of product and the pressure on particle surface was calculated by solving N-S equations based on energy and species transport equations. There is no gas flow in the closed chamber and the air diffused to particle surface and the product was released from the particle surface after reaction. The computational domain is a 40 mm \times 40 mm \times 40 mm closed space, which can supply enough air for combustion reaction. The atmosphere temperature is 1300 °C. We first statically simulated two particles aggregation. The particle diameter is 150 μ m and the particle distance also is 150 μ m. After that, the aggregation between two-particle cluster and the third particle was simulated. The third particle would aggregate from different directions to form various spatial structure and three typical positions were applied to finish this work.

3. Results and discussion

3.1. Two-particle aggregation in petcoke combustion reaction

Combustion process, to provide heat and electricity in widely industrial area, is a typical non-catalytic gas-solid chemical reaction. In our previous study [38], particle fluctuating motions induced by chemical reactions were found in petcoke combustion and gasification reactions. In this work, combustion reaction of separated petcoke particles was observed and recorded using an *in* situ reactor-high temperature stage coupled with microscope and camera as shown in Fig. 2(a). The particle diameters were about 150 μ m and the distance between these two particles was about 150 μ m as shown in the figures. In the view field of the microscope, the two particles stay static during the heating process under inert atmosphere. Aggregation of two close particles in combustion process was observed when inlet air starting the reaction as shown in Fig. 2. Figs. 2(a)-(c) show that the collision and aggregation process of two close particles was less than 0.4 s. After aggregation, combustion reaction of the two united petcoke particles proceeded. However, some of the aggregation also would disaggregate. This observation directly demonstrated particle aggregation resulting from chemical reaction.



 (1) digital camera (2) objective lens (3) cooling water inlet (4) cooling water outlet (5) gas inlet
 (6) cooling water inlet (7) gas outlet (8) cooling water outlet (9) char particle (10) sapphire slip (11) crucible (12) thermal couple (13) heating strip





Fig. 2. (a)- (c): the particle aggregation phenomenon during petcoke combustion process. (d): Schematic of combustion reaction mechanism. (e) Schematic of the concentration distribution of gas phase between two particles during the reaction process.

In the above combustion experiments, particle aggregation induced by chemical reaction was found. Herein, we analyzed the reasons for aggregations and the associated aggregation patterns. The typical non-catalytic gas-solid phase chemical reaction process was shown in Fig. 2(d) in detail. The gaseous reactant firstly diffused to the particle surface and adhered in the active sites. The chemical reaction proceeded and the product was released after reaction as shown in the figure. The relationship between surface reaction rate and reactant concentration is: $r = kc_{o2}^{n}$. The values of k (the reaction rate constant) and $n \sim 0.5$ are reported in Ref [39]. Fig. 2(e) shows schematic of the concentration distribution of oxygen and CO₂ product around solid particles. It can be easily understood that the diffusion of gaseous reactant and product is restricted because of the narrow pathway between particles. The concentration of produced CO₂ in inner side was higher than that in external side. Therefore, the oxygen concentration between two particles was extremely lower than that of external sides. The reaction rate and release velocity of gaseous product were decreased in the inner position of two particles. The non-uniform release of reaction product in different positions caused unbalanced bearing force of solid particles, which led to particle aggregation as observed in experiments.

3.2. Numerical analysis of two-particle collision and aggregation

The thin shell around the solid particle surface was chosen as the control shell at which the following chemical reaction occurs. According to the stoichiometry of the combustion reaction: $C(s) + O_2(g) = CO_2(g)$. The relationship of molar flux transfer between gaseous reactant (O_2) and product (CO_2) at the near reaction surface area of solid particle is given by:

$$\vec{lds} + \vec{r}d\vec{s} = 0 \tag{1}$$

where \vec{J} and \vec{r} are the diffusion flux (mol/s/m²) of oxygen and productive rate (mol/s/m²) of carbon dioxide, respectively. It can be found that the molar fluxes of oxygen and carbon dioxide are identical at the close particle surface area. The flow directions of oxygen and carbon dioxide are opposite to each other at near particle surface area.

Based on the principle of linear momentum conservation, the relationship between the momentum of gas and reactive force of solid particle \vec{f} is:

$$\rho \vec{u} \cdot d\vec{s} dt \vec{u} + \vec{f} dt = 0 \tag{2}$$

where ρ is the density of gas and \vec{u} is the diffusion or release velocity of gas, while t is the reaction time. The total macroscopic force acting on a solid sphere particle is zero when the reaction rate of a solid particle is uniform over different sites of particle surface. However, non-uniformity in reaction rate occurred over particle surface areas as we analyzed in Fig. 2(e). The reaction rate at different locations determine on the product release velocity on various parts of the particle surface. During the gas release process, solid particles would bear counterforce [38], which has been demonstrated in our previous study. Here, we named the force between particles as cohesive force F. The cohesive force of solid particle was contributed by oxygen and carbon dioxide fluxes according to momentum conversion. We assume the oxygen concentration in the main gas stream (air) is c_0 . The reaction rate at different reaction sites (various combination of (θ, φ) values on particle surface is given by $\vec{r}(\theta, \varphi) = kc_1^n$, where c_1 is the concentration of oxygen near particle surface. The diffusion flux of the control volume J with reference to a spherical coordinate to describe the particle is given by $\vec{J} = -D_{12} \frac{dc_1}{dr}$. Where D_{12} is the diffusivity of oxygen in CO_2 , Based on the momentum conversion Eq. (2), the reactive force

of solid particle induced from oxygen diffusion is given by $\overline{F_1}$:

$$\vec{F}_1 = \oint M_1 V_{m1} \vec{J} \cdot d\vec{s} \vec{J}$$
(3)

where M_1 is the molar mass of oxygen, V_{m1} is the molar volume at the reaction temperature and $d\vec{s}$ is the unit vector pointing outward from the reaction area of solid particle surface. At the same time, the cohesive force resulting from the release of carbon dioxide also was analyzed as \vec{F}_2 . It was assumed that the particle is spherical and reaction rate on different points of particle surface is given by $\vec{r}(\theta, \varphi)$. The reactive force induced from the release of reaction product CO₂ is:

$$\vec{F}_2 = - \oint M_2 V_{m2} \vec{r}(\theta, \varphi) \cdot d\vec{s} \vec{r}(\theta, \varphi)$$
(4)

where \vec{r} is the reaction rate per unit surface area, M_2 is the molecular weight of released CO₂, V_{m2} is the molar volume of CO₂ at the reaction temperature. Therefore, the total cohesive force on a solid particle is given by:

$$\vec{F} = \oint M_1 V_{m1} \vec{J} \cdot d\vec{s} \vec{J} - \oint M_2 V_{m2} \vec{r}(\theta, \varphi) \cdot d\vec{s} \vec{r}(\theta, \varphi)$$
(5)

The combustion reaction of two solid particles was numerically simulated using species transport model in FLUENT to understand the release of reaction product and Fig. 3(a) shows the release velocity distribution of the gaseous product (CO_2) . It was noted that the release velocity of product in the inner side is evidently lower than that in the external side. The oxygen and product concentration distributions also were shown in Fig. 3(b). The molar fraction of oxygen in the outside position is about 3 times higher than that in inner position. According to Eq. (2), the different velocity u directly results to the unbalanced force on solid particles. The varying oxygen concentration in different positions actually resulted in the variation of product release velocity and reactive force. The two-particle bearing cohesive force can be viewed as the result of asymmetrical release of reaction product. In this case, the two solid particles would aggregate together in view of the quantitative analysis given above. The gravity of a petcoke particle with 150 μ m diameter is about 1.7×10^{-8} N. The integration of pressure with particle surface showed that the reactive force of the two particles was 1.20 \times 10⁻⁸ N. It was found that the cohesive force between two particles is equal to the gravity when the particle distance is 150 μ m (center to center distance).

3.3. Three-particle aggregation phenomenon and mechanism analysis

Figs. 4(a)-(d) show four different aggregations of three solid particles during combustion process, which is similar to the previous aggregation. Some of the aggregations also would disaggregate in the combustion experiments. The observed graphs indicated that the aggregations tend to form linear structure. The observed frequency of this kind of liner structure is about 94% and detailed structure analysis also was carried out below. This phenomena also was revealed in some carbon soot aggregations according to previous studies [40]. It was reported that the reaction conditions would influence the structure of the carbon soot aggregations. However, this finding is different from carbon soot aggregation because of the different reaction processes. Carbon soot is one kind of product resulting from the oxidation process, while aggregation of solid particles reported in this study would affect the reaction kinetics. It can be found that the aggregations of three particles show a linear structure. This phenomenon is related to the combustion process, which will be analyzed and simulated below.

Based on the above analysis, particle aggregation between two particles occurred when the variation in reaction rate of different sides of particles reached the critical value. Following the two



(a) Product release velocity distribution.



(b) Product and oxygen concentration and release velocity distribution along the axis of two particles.

Fig. 3. (a) Gaseous product release velocity u in 3D combustion simulation of two separated solid particles in air atmosphere. (b) Results of product and oxygen concentration and release velocity obtained from numerical simulation.

particles aggregation, the linear aggregation structure of multiparticles also was observed according to our experiments. After understanding the aggregation mechanism of two solid particles, we analyzed three particles aggregation as shown in Fig. 5. The first two particles aggregated and continued to react with oxygen. The third particle can be aggregated from different directions. The aggregation is affected by the gas flow, which consists produced gas flow from aggregated particles and the third particle. In twoparticle aggregation, the concentration of oxygen is non-uniform around particle surfaces as shown in Fig. 5. The initial concentration of the oxygen reactant is c_0 . We divided the surface area of the aggregate into region A, named as shell area and region B, named as columnar area. The ratio of different diffusion passage areas of the two regions is calculated as shown in Eq. (6):

$$\frac{s_A}{s_B} = \frac{4\pi h^2}{2\pi h d} = \frac{2h}{d} \tag{6}$$

The diffusion passage area in region B is much lower than that in region A. In this case, the release velocity of gaseous product from the two aggregated particles in region B is higher than that in region A. Therefore, the third particle would bear significant drag force in region B, which would be difficult to aggregate with the two particles from region B for the third particle. However, particles would bear less drag force in region A because of the wider diffusion passage area. In this case, it was easier to aggregate with the two particles from region A for the third particle. Thus, the third particle would tend to aggregate with the two particles in region A resulting from the cohesive force. This explains the frequently observed linear aggregation structure of particles during reaction process.

The aggregation mechanism of the third particle contributed from region A is similar to two-particle aggregation. In region B, the drag force induced from CO₂ product release is significant and the experimental results demonstrated that the effect of gaseous product release from the aggregated particles plays a more important role in the aggregation process. The mechanism of threeparticle aggregation can also be expanded to multi-particle aggregation to explain for the liner aggregation structure. In this case, we proposed three typical types of aggregation structure named "I" structure, "L" structure and "T" structure for further numerical calculations as shown in Fig. 6(a)-(c). The judgement of the aggregate structure is decided by the degree between the collision direction and the axial direction. The threshold value of the degree is 45°, above which is the "L" structure and below this value is the "I" structure as shown in Fig. 6. The structure would be "T" form when the degree is around 135°. The "I" and "L" structure were formed by aggregating in region A and the frequency of these structures is high. However, the frequency of type "T" structure is low when



Fig. 4. (a)- (d): Four different aggregations with three solid particles during reaction process was recorded.



Fig. 5. Schematic of the oxygen concentration distribution around two aggregated particles during the reaction process.

aggregated in region B. To further demonstrate this point, we also carried out the following simulations to verify the accuracy of such a hypothesis.

3.4. Numerical analysis of three-particle collision and aggregation

Based on the above experimental and theoretical analyses, typical reaction conditions were simulated in three-dimensions as following. Combustion reaction of particles was simulated at different geometrical positions. Fig. 7 shows the numerical results of the distribution of gasification product release velocity u of different aggregates in the combustion process. It was indicated that the oxygen concentration in the inner side is lower than that in the external side, which is corresponding to our theoretical analysis as mentioned above. Therefore, reaction rate and product release velocity in the external side are stronger than that in the inner side of the aggregates as shown in Fig. 7(a)-(c). Based on Eq. (2), the reactive force of the solid particle is unbalanced and hence the particles would aggregate together with each other as found in our experiments.



Fig. 7. Product release velocity u distribution of (a) "I" aggregate, (b) "L" aggregate and (c) "T" aggregate during the combustion process.

Та	ble	2
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Comparison of simulat	ion and experimental	results for the bearing for	orce and acceleration of t	particles and aggregates.
companyon or sinnana	ion una experimental	results for the bearing h		purches und aggregates.

Classification	Bearing force F /	Bearing force F / $\times$ 10 ⁻⁸		Acceleration a /m s ⁻²	
	Particle 1	Aggregate	Particle 1	Aggregate	experiments/%
"I" structure	5.82	-6.28	32.96	-17.77	47
"L" structure	5.40	-7.57	30.57	-21.44	47
"T" structure	3.59	-3.82	20.30	-10.81	6

The values of integration of the pressure on particle surface directly reflected the bearing forces of solid particles. The detailed bearing forces of solid particles with different geometrical aggregation structures was further calculated to demonstrate the above analysis and the results are shown in Table 2. The bearing forces of the particles and aggregates was obtained from the integration of the pressure field on particle surface:  $F_{x,y,z} = \oint^{P_{x,y,z}} ds$ . The acceleration was calculated as:  $a_{x,y,z} = F_{x,y,z}/m$ . The cohesive force between the aggregate and the third particle differed from their relative position. It was concluded that the cohesive forces induced

by reaction in "I" and "L" aggregate are stronger than that in "T" aggregate. These results also demonstrated that the particles were likely to form "I" and "L" structure aggregate instead of "T" structure. This result is also corresponding to the statistic results of the repeated trials. The acceleration was calculated and the results are shown in Table 2. It was noted that the acceleration of solid particles ranged from 7.12 to 32.96 m s⁻², indicating aggregation process to occur within a short timeframe. The statistics results from the combustion experiments was compared to the simulation results as shown in Table 2. The observed frequencies



Fig. 8. Aggregate structures of multi-particles during the combustion process of petcoke particles.

of "L" and "I" aggregate structure are largely equal and the frequency of "T" aggregate structure is merely about 6% in combustion experiments of petcoke. The frequencies of "L" and "I" structures were much higher than that of "T" structure in experiments, which indicated that particles tends to form liner structure instead of group structure. This result also demonstrated the reliability of conclusions obtained from simulation works. Following the threeparticles aggregation, more particles aggregation and liner structure were observed as shown in Fig. 8(a) and (b). The first three particles formed "I" structure and then the following particle aggregated with the three particles to show "L" structure. This complex structure also was named as dendritic or structure in some references [29,41]. Particle aggregation during the combustion process tend to form this kind of dendritic structure, which is similar to the carbon soot aggregation.

## 3.5. Forces acting on particles may result to aggregation

Other forces acting on particles aggregation consist Van der Waals forces, liquid bridge force, drag force, gravity, electrostatic force, et al. Herein we analyzed these forces one by one and compared with forces induced by chemical reactions. In this work, the reaction temperature is 1300 °C and the liquid bridge force induced by moisture can be neglected. The particles were placed in a small heating crucible and the drag force induced by inlet gas flow also is negligible. The direction of the gravity is perpendicular to the moving direction of particles and makes no influence in this work. The Van der Waals forces  $F_{cw}$  can be given by [42]:

$$F_{cw} = \frac{hWR}{8z_0^2} \tag{7}$$

where  $z_0$  is the particle distance and the Van der Waals force is significant when the values of  $z_0 \ll R$  or  $z_0 < 0.4$  nm [43,44], and *R* is the particle radius. Thus, the Van der Waals force only make a difference when the particles aggregated together. This force promoted the disaggregation of clusters. However, the magnitude of Van der Waals force between micro-particles is  $10^{-10}$  N [44,45], which is negligible compared with the reactive force induced by chemical reaction. Similarly, the electrostatic force  $F_e$  acting between electrically charged particles can be obtained by Coulomb's law:

$$F_e = \frac{1}{4\varepsilon\pi} \frac{Q_1 Q_2}{z_0^2} \tag{8}$$

where  $\varepsilon$  is the permittivity of the surrounding medium,  $Q_1$  and  $Q_2$  are the electric charge of solid particles. In this study, the petcock particles were believed without electrically changed. Therefore, the electrostatic force between particles is not considered.

From the above analysis, we can found that only the Van der Waals forces could make effect when particles aggregate together and it can be neglected in the collision and aggregation process. Besides, the Van der Waals forces can restrain the disaggregation of solid particles.

## 4. Conclusions

In Conclusion, particle collision and aggregations were experimentally and numerically investigated. Chemical reaction induced particle aggregations were found in non-catalytic gas-solid phase combustion reaction process. The mechanism of this aggregations is the asymmetry of gaseous concentration around solid particles, which leads to the different reaction rates in various regions on particle surface. Therefore, the force resulting from the release of product is non-uniform on particle surface. For the two-particle case, the reactant concentration between particles is lower than the outside region. Two particles bore cohesive force and particle aggregation phenomenon occurred under this condition. The spatial structure of the multi-particle aggregations tends to show a liner structure. Particles also bear drag force due to the release of product from the aggregate surface. What's more, the drag force is more significant as compared with the cohesive force when the third particle is in the vertical position. In this case, the third particle tends to aggregate from the parallel direction of the aggregates and forms into a liner structure. The simulation of combustion reaction also demonstrated that different reactant concentration distribution around particles resulted in various aggregates of two and three solid particles.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## APPENDIX A: AGGLOMERATING FORCE ANALYSIS

According to the momentum conservation:

$$m\vec{u} + \vec{f}dt = 0 \tag{A1}$$

Where *m* is the mass of gas (reactant  $O_2$ , product  $CO_2$ ) and  $\vec{u}$  is the diffusion  $(O_2)$  or release  $(CO_2)$  velocity of reactant and product gas,  $\vec{f}$  is the reactive force of solid particles.

$$m = \rho \vec{u} \cdot d\vec{s} dt \tag{A2}$$

where  $\rho$  is the density of the gas.

 $\rho \vec{u} \cdot d\vec{s} dt \vec{u} + \vec{f} dt = 0$ (A3)

$$\rho \vec{u} \cdot d\vec{s} dt \vec{u} = -\vec{f} dt \tag{A4}$$

Applying Eq. (A3) in the diffusion process,

$$\rho \vec{u} \cdot d\vec{s} dt \vec{u} = -M_1 \vec{J} \cdot d\vec{s} dt V_m \vec{J} \tag{A5}$$

where  $\vec{J}$  is the unit velocity in the diffusion direction, which is aligned along with the particle radial direction pointing towards the center of the particle. Checking on the dimensions of Eq. (5):

$$kgm^{-3}.m^{2}s^{-2} = mol^{2}m^{-4}s^{-2}.kgmol^{-1}.m^{3}mol^{-1}$$
(A6)

$$\vec{F_1} = \oint M_1 V_{m1} \vec{J} \cdot d\vec{s} \vec{J}$$
(A7)

Similarly, applying Eq. (3) on the release of product in reaction process.

$$\rho \vec{u} \cdot d\vec{s} dt \vec{u} = M_2 V_m \vec{r}(\theta, \varphi) \cdot d\vec{s} dt \vec{r}(\theta, \varphi)$$
(A8)

 $kgm^{-3}.m^2s^{-2} = mol^2m^{-4}s^{-2}.kgmol^{-1}.m^3mol^{-1}$ (A9)

$$\vec{F}_2 = - \oint M_2 V_{m2} \vec{r}(\theta, \varphi) \cdot d\vec{s} \vec{r}(\theta, \varphi)$$
(A10)

where  $\vec{r}$  is the release rate of the product, which is equal to the reaction rate. The direction is opposite to the particle radial direction towards the particle center. Therefore, the reactive force  $\vec{F}$  of solid particles induced by diffusion and product release is given by:

$$\vec{F} = \oint M_1 V_{m1} \vec{J} \cdot d\vec{s} \vec{J} - \oint M_2 V_{m2} \vec{r}(\theta, \varphi) \cdot d\vec{s} \vec{r}(\theta, \varphi)$$
(A11)

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