JEAS

JOURNAL OF ENGINEERING
AND
APPLIED SCIENCES

Journal of Engineering and Applied Sciences 12 (2018), 1-10

Particle-Particle Interactions in Sub-Bituminous Coal Powder Agglomerates: Surface Thermodynamic Approach

Ikebudu K. O[1*], Omenyi S. N[2] and Achebe C. H[3]

[1]Department of Mechanical Engineering, COOU - Chukwuemeka Odumegwu Ojukwu niversity, Anambra State, Nigeria, ikbuduk@yahoo.com
[2] Department of Mechanical Engineering, Nnamdi Azikiwe University, Anambra State, Nigeria, sam.omenyi@unizik.edu.ng
[3] Department of Mechanical Engineering, Nnamdi Azikiwe University, Anambra State, Nigeria, Ch.achebe@unizik.edu.ng

*Corresponding Author’s E-mail: ikbuduk@yahoo.com

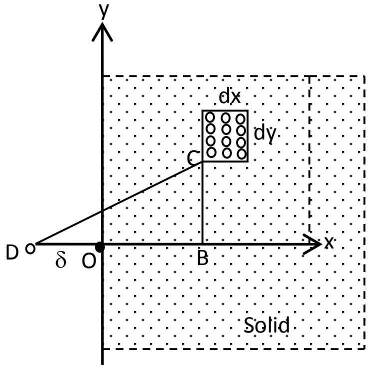
Abstract
This paper presents particle-particle interactions in sub-bituminous coal powder agglomerates employing surface thermodynamics approach. The coal was ground in a dry state with a milling machine into powder form and sieved with Octagon 2000 sieve shaker of size range 75μm - 850μm. The coal powder (0.01404kg) was mixed with about 1.3cm^3 of 50% ethanol which served as a binder. Also the binding forces of agglomerates were determined with the binding force model. The Lucas-washburn equation was used to determine the contact angle ($\theta = 64.8^\circ$) of sub-bituminous coal. 0.0361Jm^{-2} and 0.0324Jm^{-2} were determined as the surface energy and interfacial tension of sub-bituminous coal respectively. The values of Hamaker coefficient in a medium $A_{131} = 1.201\times10^{-20}$Jouls was obtained using the values of surface tension of binder, contact angle, Neumann equation, MATLAB fzero command and combination rule. The positive value of Hamaker coefficient, which implies net positive van der Waals forces shows an attraction between two particles. The outcome of this study would improv fugitive dust control, decrease transportation losses and lower risk of spontaneous combustion of coal agglomerates. The theory of van der Waals effect was successfully applied to the study of particle-particle interactions in the agglomeration of coal.

Keywords: Sub-Bituminous Coal, Surface tension, Contact angle, Hamaker Coefficient, Binding force

1. Introduction

Binding force of coal powder agglomerates not only ensures a further applicability and processing of coal but leads to improved fugitive dust control, decreased transportation losses and lower risk of spontaneous combustion. Binding agents agglomerate fine loose particles by adhesion. In most cases, hydrophobic condition is preferable because they form material bridge between the particles. The optimum binder combination for mechanical properties, operational cost and availability are molasses, ethanol and line. Nevertheless, any of these binders can be used to achieve effective agglomeration. In this work, ethanol of different concentrations will be used as binder. Agglomeration improves some mechanical properties of coal and enhances its handling. The phenomenon of agglomeration usually involves wetting, spreading, nucleation, consolidation and coalescence. The moist agglomeration process is realized through a series of four states of pendular, funicular, capillary and droplet. Some fine grain cannot be used for industrial purposes; therefore, must be pelletized with binders. The improved properties of agglomerates can be attributed to the van der waals force, which arises from the interaction of oscillating dipoles. This attractive force can be quantified in the light of Hamaker constant. Studies have shown that agglomeration improves both the mechanical and physical properties of the fine grains. A proper understanding of the behaviours and kinetics of the coal agglomerates are important for better application.

Van der Waals forces exist not only between individual atoms and molecules but also between particles. Hamaker, (1937) used the additivity concept proposed by London (1936) to determine the equation for the van der Waals force between particles. The additivity concept allows the force to be calculated based on the interaction between individual atoms making up the particles. Consider the interaction between a molecule and a solid body of infinite extent bounded by a plane surface which is made of the same molecules, as shown in Fig 1.



OB = x

BC = y

DO = δ

CD = $[(\delta + x)^2 + y^2]^{1/2}$

Fig.1: Interaction between a molecule and a planar half-space

This work investigated the particle-particle interactions in coal powder agglomerate using surface thermodynamics approach. This work introduced application of the van der Waals interaction effect in particle-particle interactions in the agglomeration.

2.0 Material and methods

2.1 Governing Equations

The coal particles used in this work are from Sub-bituminous coal. It was obtained from Enugu State, Nigeria. 50% ethanol-water mixture was used as a binder for particle-particle agglomeration. The Sub-bituminous coal was ground dry (with a milling machine) into powder form and sieved with standard mechanical shaker Octagon 2000. The standard sizes of the shaker are of the range 75µm, 150 µm, 212µm, 300µm, 425µm and 850µm meshes. The coal particles were agglomerated with the use of balling disc machine.

The net interaction energy E of the molecule D at a distance, δ away from the surface is given as eqns 1a and 1b

$$E = -2\pi q L \int_o^\infty dx \int_o^\infty \frac{y\,dy}{[(\delta+x)^2+y^2]^3} \qquad (1a)$$

$$E = -\frac{\pi q Lc}{6\delta^3} \qquad (1b)$$

The force F is given by

$$F = -\frac{dE}{d\delta} = -\frac{\pi q Lc}{2\delta^4} \qquad (2)$$

where Lc is the London constant, q is number of molecules per unit volume.

Following a similar procedure, the expression for the interaction energy for some simple shapes can be derived. For instance, the van der Waals interaction energy per unit area between two blocks of the same material at distance δ apart is given by Hamaker (1937).

$$E = -\frac{\pi q^2 Lc}{12\delta^2} \qquad (3)$$

The quantity $\pi^2 q^2 Lc$ is known as Hamaker constant (A). If the interaction between the molecules of different materials is being considered then,

$$A = \pi^2 q_1 q_2 Lc_{1,2} \qquad (4)$$

Therefore, equation (3) can be written in terms of Hamaker constant as,

$$E = -\frac{A}{12\pi\delta^2} \qquad (5)$$

The ratio of the Van der Waals force between a sphere and planar half-space, and the interaction energy (per unit area) between plane parallel half-space is

$$E_{sp} = -\frac{AR_S}{6\delta} \tag{6}$$

Where Rs is the radius of the sphere and δ is the separation distance between the surfaces.
The force of interaction is given by

$$F_{sp} = \frac{dE_{sp}}{d\delta} = -\frac{AR_S}{6\delta^2} \tag{7}$$

The interaction energy per unit area between parallel half-spaces, E_{pp} is given by (Hamaker 1937)

$$E_{pp} = -\frac{A}{12\pi\delta^2} \tag{8}$$

Therefore,

$$\frac{F_{sp}}{E_{pp}} = 2\pi R_S \tag{9}$$

The force between two spheres can be expressed in terms of Epp as,

$$F_{ss} = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)E_{pp} \tag{10}$$

Equation (10) can be written as

$$F = \frac{AR}{12\delta^2} \tag{11a}$$

Hamaker coefficient, A, depends on the macroscopic material properties of the interacting particles $\mathbf{A_{131}}$. to be determined. So equation (11a) becomes

$$F_{131} = \frac{A^{(131)}}{12\delta^2}r \tag{11b}$$

$$F_{131} = \frac{A^{(131)}}{12\delta^2}r\ x\ (1-\varepsilon) \tag{12}$$

Where R equals the reduced radius or

$$R = \frac{2R_1R_2}{R_1+R_2} \tag{13}$$

Equation (11b) is the van der Waals force of attraction between two sphere particles.
This approach assumes complete additivity of force between individual particles and is called the microscopic approach to van der Waals forces.

The Tensile and Compressive strengths are respectively more amenable to theoretical and experimental analysis. Consideration of both is thus normally needed in complete analysis of agglomerate strength. Rumpf, (1962) gives the following theoretical equation
For tensile strength;

$$\sigma_T = \frac{9}{8}\frac{1-\varepsilon}{\pi d^2}k_nH \tag{14}$$

Where k_n represents the coordination number and H is the tensile strength of a single bond. The void fraction or porosity ε been correlated experimentally by Rumpf (1962) as $k_n\varepsilon = \pi$. Equation (14) thus becomes

$$\sigma_T = \frac{9}{8}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{H}{d^2} \tag{15}$$

It can be assumed that the inter-particle binding force F Rumpf, (1962) is given by

$$F = \frac{\pi d^2}{4}H \tag{16}$$

Then eqn. (15) becomes

$$\sigma_T = \frac{9}{8}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{4F}{\pi d^4} = \frac{9}{2}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{F}{\pi d^4} \tag{17}$$

The interaction energy of spherical particles 1 and 2 of respective radii r_1 and r_2 separated by a distance δ in medium 3 is given by Rumpf (1962) as

$$\emptyset_{132} = \frac{-A^{(132)}}{6\delta}\left(\frac{r_1r_2}{r_1+r_2}\right) \tag{18a}$$

The case where the particles are identical Rumpf (1962) gives

$$\emptyset_{131} = \frac{-A^{(131)}}{12\delta}r \tag{18b}$$

Where r is the common radii of the identical particles. The interaction or binding force between the particles become

$$F_{131} = \frac{d\emptyset_{131}}{d\delta} = \frac{A^{(131)}}{12\delta^2} r \qquad (19)$$

Eqn. (19) is inserted in eqn. (17) to give

$$\sigma_T = \frac{9}{48}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{A^{(131)}}{\pi d^3 \delta^2} \qquad (20)$$

Suppose the relation between σ_T and the compressive strength σ_C is given by $\alpha(\sigma_T) = {}^{\sigma_T}/_{\sigma_C}$ (Rumpf 1962); and (Orr 1966) where α is presumed to be a function of σ_T then eqn. (20) becomes

$$\sigma_C = \frac{9}{24}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{A^{(131)}}{\pi d^3 \delta^2}\left(\frac{1}{\alpha(\sigma_T)}\right) \qquad (21)$$

The Hamaker coefficient A_{132} for two macroscopic particles 1 and 2 interacting across a medium 3 can be estimated with the combination rule

$$\mathrm{A}_{132} \approx (A_{11}^{0.5} - A_{33}^{0.5})(A_{22}^{0.5} - A_{33}^{0.5}) \qquad (22)$$

The Hamaker coefficient $\mathrm{A}_{\mathrm{i3i}}$ for two identical macroscopic particles 1 and 1 interacting across a medium 3 (ethanol-water mixture, 50-50 by volume) becomes

$$\mathrm{A}_{\mathrm{i3i}} \approx \left(A_{ii}^{0.5} - A_{33}^{0.5}\right)^2 \qquad (23)$$

Where A_{ii} where i= 1, 2 and 3 is the Hamaker constant of material i in vacuum. An approximate equation giving A_{ii} as a function of free surface energy γ_i for solids is seen in Lefevre G. and A. Jolivet (2009)

As $\mathrm{A}_{\mathrm{ii}} = 24\pi \mathrm{D}_0^2 \gamma_i = 2.1 \times 10^{-21}\gamma_i$ (24)

Recall that Young's equation is

$$\gamma_{sv} - \gamma_{sl} - \gamma_{lv}cos\theta = 0 \qquad (25)$$

Normally θ is measurable and γ_{lv} is known meaning that equation (25) is one equation in two unknowns. Additional equation is furnished by equation of state which states that the interfacial energy γ_{sl} is completely described with the knowledge of the free surface energies γ_{sv} and γ_{lv}. The equation of state is generally represented in mathematical form as

$$\gamma_{sl} = f(\gamma_{sv}, \gamma_{lv}) \qquad (26)$$

A popular equation of state formulated by Neumann et al (1974) is

$$\gamma_{sl} = \frac{\left(\gamma_{sv}^{0.5} - \gamma_{lv}^{0.5}\right)^2}{1 - 0.015(\gamma_{sv}\gamma_{lv})^{0.5}} \qquad (27)$$

Simultaneous solution of equation (25 &27) leads to the surface energies; γ_{sv} and γ_{sl} associated with the solid. Using equation (27) the interfacial energy γ_{sl} is eliminated from equation (25) to give the single-variable equation

$$\gamma_{sv} - \frac{\left(\gamma_{sv}^{0.5} - \gamma_{lv}^{0.5}\right)^2}{1 - 0.015(\gamma_{sv}\gamma_{lv})^{0.5}} - \gamma_{lv}cos\theta = 0 \qquad (28)$$

Inserting surface tension of liquid γ_{lv} and contact angle θ in equation (28) for the case of sub-bituminous coal, the arising non-linear equation will be resolved with MATLAB fzero command which will give surface energy $\gamma_{sv} \equiv \gamma_{s-bcv}$ and interfacial tension between solid and liquid $\gamma_{sl} \equiv \gamma s_{s-bcl}$.

The common radii r of the identical particles is determined from the particle size and the minimum separation $\delta\ or$ d_0 betwwen two spheres is presumed as 1.82 Å = 2Å which is from (Omenyi etal 1979 and 1982).

Suppose it is presumed that $\gamma_i = \gamma_{iv}$ then the Hamaker constants in a vacuum for the coal types studied in this project becomes

$$\mathrm{A}_{s-bc,s-bc} = 2.1 \times 10^{-21}\gamma_{s-bcv}$$

In this study, electrostatic forces were not considered because bridging liquid is not ionic. In the determination of the contribution of van der Waals forces, the surface tension data and contact angle were used with the relevant equations.

To calculate the interaction or binding force and strength between the particles, eqn. (11b) was used thus;

$$F_{131} = \frac{d\emptyset_{131}}{d\delta} = \frac{A^{(131)}}{12\delta^2} r$$

3.0 Results and Discussions
3.1 Surface Free Energy Determination

To determine A_{i3i}, equation (15) is used; where
$A_{ii} = 2.1 \times 10^{-21}\gamma_{s-bcv}$ and $A_{33} = 1.411 \times 10^{-20}$J
Noting that, according to Spagnoli et al (2011), the value of A_{33} for ethanol-water mixture (50-50 by volume) is 1.411×10^{-20}J.
Inserting $\gamma_{lv} = 0.04764$Jm^{-2} and θ = 64.8° in equation (20) for the case of sub-bituminous coal and solving the arising non-linear equation with MATLAB fzero command gives surface energy $\gamma_{sv} \equiv \gamma_{bcv} = 0.0361$ Jm^{-2} and interfacial tension between solid and liquid $\gamma_{sl} \equiv \gamma_{bcl} = 0.0324$ Jm^{-2} .
Suppose it is presumed that $\gamma_i = \gamma_{iv}$ then the Hamaker constants in a vacuum for the coal types studied in this project becomes
$A_{s-bc,s-bc} = 2.1 \times 10^{-21}\gamma_{s-bcv}$
$= 2.1 \times 10^{-21} \times 0.0361$
$= \mathbf{7.581 \times 10^{-23}J}$

To determine the Hamaker Coefficient A_{131} of sub-bituminous Coal Agglomerates; according to Giovanni et al (2011), the value of A_{33} for ethanol-water mixture (50-50 by volume) is 1.411×10^{-20}J. Making use of equation (15), the Hamaker coefficient A_{131} between the liquid and the solid for the sub-bituminous coal becomes
$A_{s-bc3s-bc} = \left(A_{s-bc,s-bc}^{0.5} - A_{33}^{0.5}\right)^2$
$= \left((7.581 \times 10^{-23})^{0.5} - (1.411 \times 10^{-20})^{0.5}\right)^2$
$= \mathbf{1.201 \times 10^{-20}J}$
The Hamaker constants in a vacuum for sub-bituminous coal is 7.581×10^{-23}J. Note that sub-bituminous coal is denoted as $A_{s-bc,s-bc}$. Applying equation (23), $\mathbf{1.201 \times 10^{-20}J}$ was determined as the Hamaker coefficient A_{131} in a medium for sub-bituminous coal. This value was compared with the values (1.411×10^{-20}J) obtained by Spagnoli et al (2011).

3.2 Particle –Particle Interactions

The particle sizes, determined inter-particle spacing, binding force *F* and agglomerates strength can be seen in the table 1;

Table 1: Agglomerates particles results of sub-bituminous coal

Particle size (μm)	Inter-particle spacing δ (Å)	Binding force F_{131}(J/m − 2)	Agglomerates Strength $\sigma_{t(N/m2)}$
75μm	1.82	1.1330×10^{-23}	6.5283×10^{-28}
150μm	1.82	2.2661×10^{-20}	8.1604×10^{-29}
212μm	1.82	3.2027×10^{-20}	6.9641×10^{-45}
300μm	1.82	4.5322×10^{-20}	1.0200×10^{-29}
425μm	1.82	6.4206×10^{-20}	3.7367×10^{-30}
600μm	1.82	9.0644×10^{-20}	1.2244×10^{-30}
850μm	1.82	1.2841×10^{-19}	4.6709×10^{-31}

The binding force *F* and agglomerates strength in table 1 was determined from the developed models. The reason of bringing together these parameters is to show and observe the correlational behaviour of particle – particle interactions and to know the type of energy that exist in the particle curves.

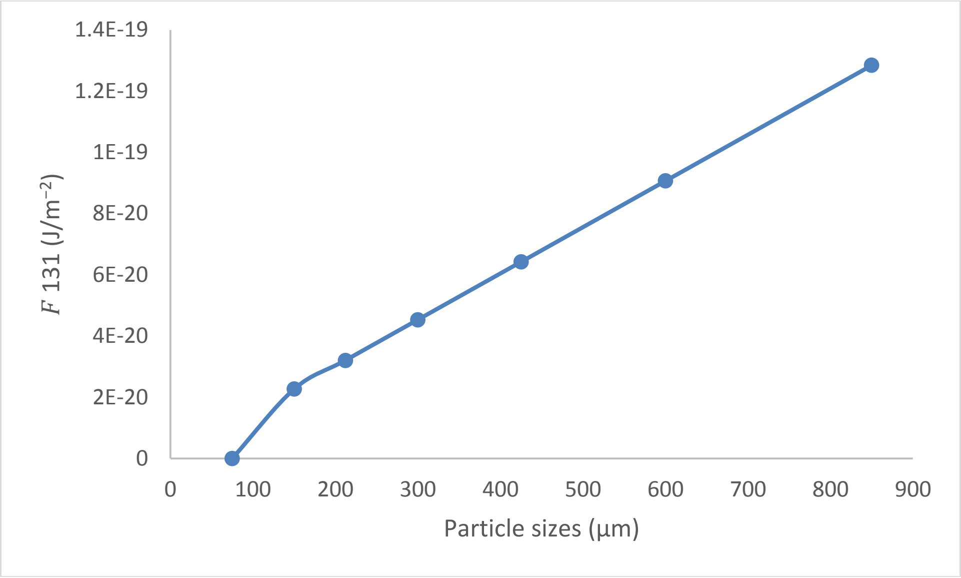


Figure 2: Particle-Particle interaction: F 131 (J/m^{-2}) versus Particle sizes (µm) of Sub- Bituminous Coal Agglomerates.

The plot in figure 2 presents the Particle-Particle interaction: F 131 (J/m^{-2}) versus Particle sizes (µm) of Sub-Bituminous Coal Agglomerates. As the Particle size (µm) is increasing, the binding force F 131 (J/m^{-2}) is equally increasing. In figure 1, there was a sharp increase in binding force F 131 (J/m^{-2}) from 75µm of Particle size to 150µm of Particle size and consequently there was a gradual smooth increase in the value of binding force F 131 (J/m^{-2}) as the particle size increases. The implication is that larger particle sizes require greater force to be agglomerated together. As the sizes move from Nano scale - micro scale and to macro scale, particle-Particle interactions are gradually reduced requiring more force to hold them together as one unit (pellet). Thus, Nano particles require less force for agglomeration while macro particles will require greater force of agglomeration.

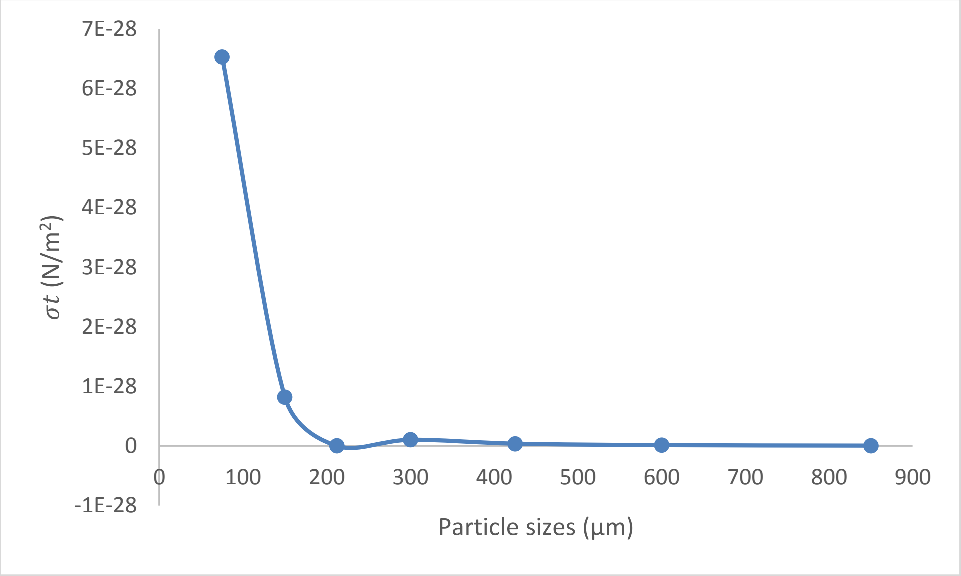


Figure 3: Particle-Particle interaction: σt (N/m^2) versus Particle sizes (µm) of Sub-Bituminous Coal Agglomerates.

In figure 3, it presents the Particle-Particle interaction: σt (N/m^2) versus particle sizes (µm) of sub-bituminous coal agglomerates. In figure 3, there was a sharp drop in the stress value from 75µm of Particle size to 150µm of Particle size and then relative constant stress level maintained as the particle size increases. As the agglomerates strength σt

(N/m^2) increases, the particle size tends to decrease. Figure 3 takes the shape of a potential energy curve for two particles showing a potential well at point of minimum energy at a given particle size of 200µm.

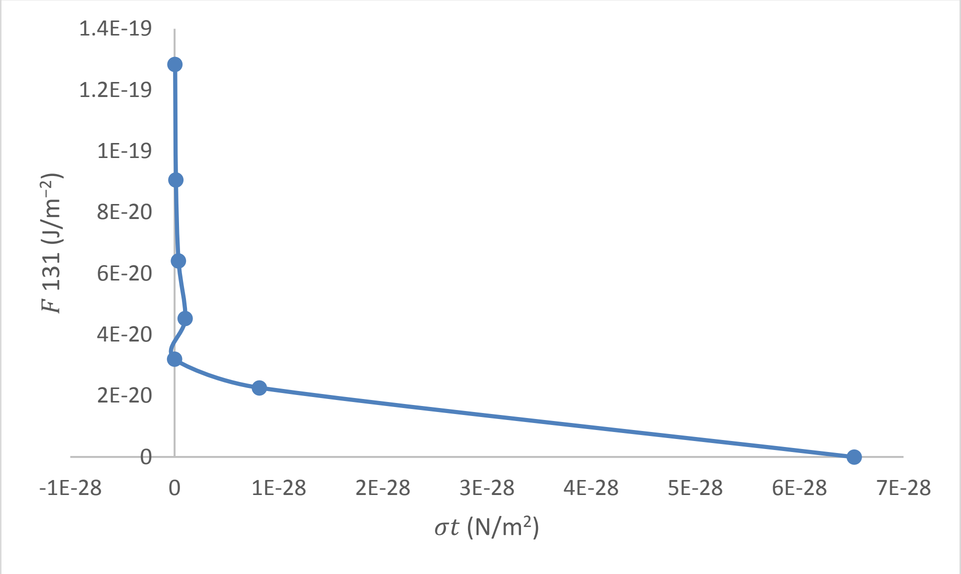


Figure 4: Particle-Particle interaction: F 131 (J/m^{-2}) versus σt (N/m^2) of sub-bituminous coal agglomerates.

Figure 4 presents Particle-Particle interaction: F 131 (J/m^{-2}) versus σt (N/m^2) of Sub-Bituminous Coal Agglomerates. As the stress increases, the binding force decreases. Naturally, force is supposed to increase as stress increases, but as a result of particle size, the reverse is the case. It means that smaller particle sizes gave rise to high stress value.

4.0. Conclusion

This research concludes that van der Waals force of attraction exists in the particle-particle interactions in the agglomeration of coal particles. This work introduced, the application of the van der Waals interaction effect in particle-particle interactions in the agglomeration of coal particles. Nano particles requires lesser force for agglomeration while macro particles requires greater force of agglomeration. Industries are advised to agglomerate from Nano scale - micro scale to ensure better binding at lower cost.

References

Hamaker, H.C. (1937) The London-Van der Waals Attraction between Spherical Particles, Physica IV, No. 10, 1058.

Lefevre G. and A. Jolivet (2009) Calculation of Hamaker constants applied to the deposition of metallic oxide particles at high temperature. Proceedings of International Conference on Heat Exchanger Fouling and Cleaning VIII. H. Muller-Steinhagen, M. R. Mlayeri and A. P. Watkinson.http://www.heatexchanger-fouling.com.

Neumann A.W., R.J. Good, C.J. Hope, M. Sejpol, (1974) An equation-of-state approach to determine surface tensions of low-energy solids from contact angles. Journal of colloid and interface science, 49. 291-304. http://www.researchgate.net/publication/256218241_An_Equation-of-State_Approach_to_Determine_Surface_Tensions_of_Low-Energy_Solids_from_Contact_Angles.

Omenyi, S. N., A. W. Neumann, and C. J. van Oss. (1979). Negative Hamaker coefficient I. Particle engulfment or rejection at solidification fronts. Colloid & Polymer Sci. 257, 413 - 419

Omenyi, S. N., A. W. Neumann, and C. J. van Oss. (1982). Attraction and Repulsion of Solid Particles by Solidification Fronts. 3. Van der Waals Interactions. Journal of Physical Chemistry 86, 1267

Rumpf H. (1962). The strength of granules and agglomerates, in W. A. Knepper (Ed), Agglomerates, Interscience, New York, pp. 379-414.

Spagnoli Giovanni, Helge Stanjek, Asuri Sridharan. (2011) Influence of ethanol/water mixture on the undrained shear strength of pure clays, 70(1). DOI 10.1007/s10064-011-0393-4. Bull Eng Geol Environ.