

Selection of Appropriate Model for the Synthesis of Coal Water Slurry (CWS) Using PVA and TEA

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ABSTRACT: Coal-Water Slurry (CWS) is an attractive alternative fuel with lower cost and reliable in terms of transportation and handling. The efficiency of CWS gasification depends on the preparation of CWS to ensure the higher carbon contents and low viscosity which will enhance the heating rates along with the atomization of CWS. In this paper, the rheology of CWS was studied with coal loading 30 to 60% and the rheological behavior was discussed with the help of Power-law, Casson and Herschel Buckley models which shows that CWS exhibits pseudo-plastic (shear thinning) behavior. The CWS was prepared by using Poly-Vinyl Alcohol (PVA) and Triethanol Amine (TEA) as dispersants and Xanthan gum as a stabilizer. The experimental results showed that for a constant coal loading viscosity decreases as the shear rate increases and out of these rheological models, power-law fits best on the experimental data with the highest R^2 of 0.99.

KEYWORDS: Coal preparation; Coal water slurry; Rheology; coal gasification.

INTRODUCTION

Coal-Water Slurries (CWSs) are gaining worldwide importance for its use as an alternative fuel. This grasps the attention of the researchers due to the rapid depletion of oil reservoirs throughout the world. CWS is referred

to as an alternative fuel as well as environmental-friendly fuel in terms of low emission of pollutants [1]. Several studies have been conducted which shows that the concentrations of dangerous emissions from the combustion of coal

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water slurry using Petrochemicals are not worst as pulverized coal [2]. The production of SO_x, NO_x, CO₂, and CO is also significantly low at low combustion temperature in CWS. Furthermore, the wide use of coal water slurry as fuel is cheap and beneficial in terms of both energy output and ecology [3-5].

The coal and water together form an unstable and complex mixture. It is prepared by suspending fine particles of coal in water. Coal is hydrophobic in nature and the fine particles of coal are forced to be dispersed in water by using dispersing agents. Since CWS works as a fuel, therefore, the most important requirement is that the coal concentration should be made as high as possible, but the viscosity should be kept at a minimum level for ease of handling, transportation, and atomization [6]. The viscosity of the slurry increases with solid concentration. Therefore, the concentration of the coal and viscosity should be optimized for the efficient combustion of the CWS [7-12]. Hence, it is important to identify rheological characteristics that lead to increasing of dilatancy or pseudo-plasticity at increased shear rates. The availability of this information will make it possible to optimize fuel slurry formulations, achieving high solids concentration. This will give high energy density and the low apparent viscosity at different shear rates, leading to better atomization quality and better combustion performance.

The rheological behavior of CWS, the effect of particle size distribution, effect of pH, effect of temperature, effect of coal loading and use of additives to reduce the viscosity and increase the stability of CWS, and modelling of the flow behavior have been investigated by numerous researchers [11, 13-16]. However, there is a gap in finding out the best suitable model amongst different rheological models by comparing them. The rheological models help in computing different parameters i.e. viscosity at different shear stress and pressure drop which makes easier for the analysis and ability of the fluid to perform specific functions. The most frequently used models are the Power-law & Bingham models that are two parameters model [17]. Some other models used three parameters for the flow characteristics of the fluid in the upper and lower Newtonian regions with the Power-law region.

Herschel Buckley model helps in the identification of the yield stress that the CWS requires to flow whereas, Casson model used to express the non-Newtonian

behavior with the yield stress of the CWS [18, 19]. The coal particles are hydrophobic in nature since they repel water molecules and therefore the coal particles forced to disperse in water by attractive and repulsive forces. Hence, the rheological behavior and stability of the slurry is strongly dependent on the chemical interaction between the particles [2].

This work reports a clear and thorough study on the effect of PVA and TEA on the rheological behavior of CWS with different coal loadings. The rheological behavior of the slurry was analysed by different rheological models to determine the best-fit model that accurately represents the behavior of CWS.

EXPERIMENTAL SECTION

Materials

The Proximate and Ultimate analysis of Lakhra coal Pakistan is mentioned in Tables 1 & 2.

Coal Water Slurry (CWS) Preparation

The 12-14 cm size pieces of lignite type Lakhra coal were taken from Fuel Research Centre (FRC) of Pakistan Council of Scientific and Industrial Research (PCSIR). In first phase, the coal was crushed manually by hammering the large chunks into smaller pieces of size 2-3cm, and then the coal ground in Hammer mill, which operates at 2800 Rpm, then the separation of 75-95 microns coal particles was done by using Vibratory sieve apparatus.

This pulverized coal was added in water for the making of CWS as shown in Fig. 1 (a). Dispersing and stabilizing agents were added as less than 2% of the solution, which modified the suspension behavior and binds coal with water molecules. PVA and TEA were used as dispersing agents and Xanthan gum was used as stabilizing agent as shown in Fig. 1 (b). The coal loading was varied from 30% to 60% keeping the number of additives constant as shown in Table 3.

Rheological measurement

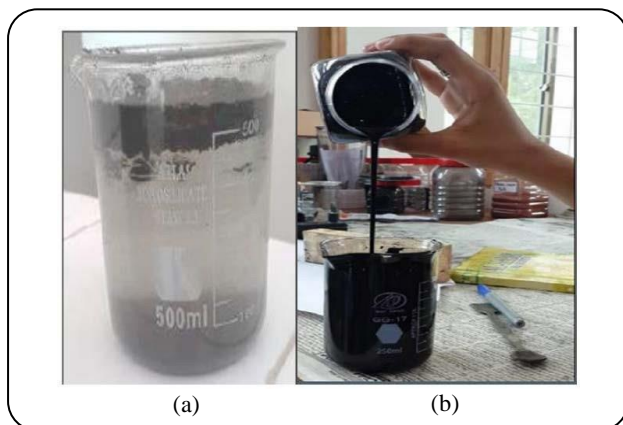
The rheology of the coal suspension depends on the inter particle attractive forces; these in term depend on the chemical structure of the surface, which is specific to coal and total surface area, which can be inferred from its concentration in the suspension and the particle size distribution. The rheological testing of CWS was carried out by using BROOKFIELD DV-E viscometer.

Table 1: Proximate Analysis of Coal.

Moisture (%)	15
Volatile Matter (%)	33
Ash (%)	10
Fixed Carbon (%)	20.7

Table 2: Ultimate Analysis of Coal.

Carbon (%)	38.04
Hydrogen (%)	4.43
Nitrogen (%)	0.79
Oxygen (%)	7.74
Sulfur (%)	1.8
Calorific Value (kcal/kg)	2540-4200

**Fig. 1: Coal water without additive (a) and coal water with additive (b).**

The experiment was performed on spindle 2 at room temperature and viscosity readings were noted after every 10 minutes of rotation at different rpm as shown in Table 4. The shear stress and shear rate were calculated by using Mitschka's method [20].

Common Rheological models

The rheological model for non-Newtonian fluids is the Power-law model, Casson model, and Harshel Buckley model, respectively as shown in Equations (1), (2) & (3). The comparisons of these models are used to analyse the rheological behavior of slurry.

Power-law Model

$$\tau = k\dot{\gamma}^n \quad (1)$$

Where, k =consistency, n = Power-law index.

Casson Fluid Model

$$\tau^{0.5} = k_0 + k_1 \dot{\gamma}^{0.5} \quad (2)$$

Where k_0 shows square root of yield stress and k_1 shows consistency factor.

Herschel Buckley Model

$$\tau = \tau_{OH} + k\dot{\gamma}^n \quad (3)$$

Where, k = consistency; n = Power-law index and τ_0 = yield stress.

RESULTS AND DISCUSSION

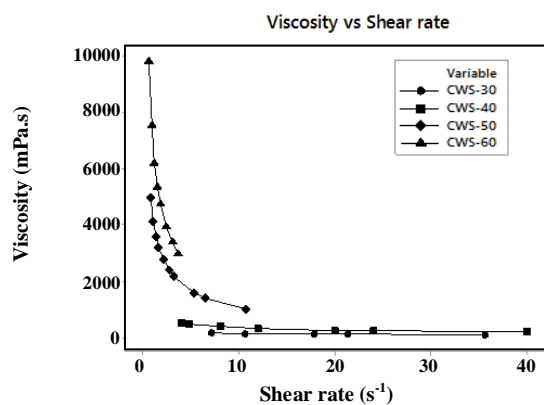
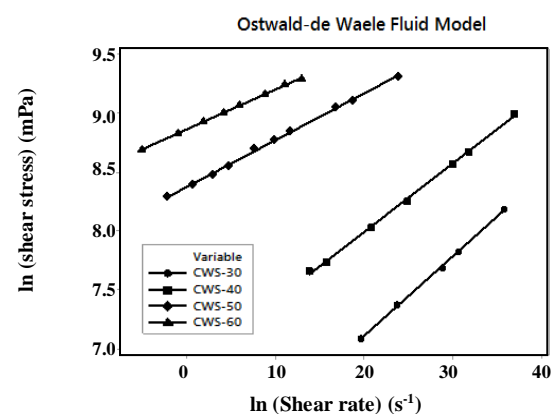
The main function of the dispersing agent is to reduce the viscosity of slurry [21]. In this study, PVA and TEA both are used as dispersing agents. PVA is most commonly used as a dispersing agent. It has both hydrophilic and hydrophobic parts and it is non-ionic in nature. The large non-ionic polymer chains of PVA adsorbed on the surface of coal particles and prevents particle aggregation. When two particles approach each other, the polymer chains begin to overlap, so the polymer chains act as a shell around the particles and hence decreases the interparticle interaction strength and reduces the viscosity [22-28]. The Small amount of TEA is also added as dispersant in slurry. TEA is normally used as dispersing agent, lubricating agent and as pour point reducer in oil treatment [28,29]. It is also used in the separation of SO_x, NO_x, and CO₂, from flue gases so it may help in reducing the emission of these gases. Though it is hydrophilic in nature, it spontaneously adsorbed to hydrophobic surface in water which results in decreasing the interfacial free energy and viscosity because adsorption is directly related to decrease in viscosity and interfacial free energy [23-27]. Fig. 2 shows that as the coal loading increases the viscosity of the slurry increases but the viscosity of coal water slurry decreases with the increased shear rate, which is basically a pseudo-plastic behavior [2, 29, 30]. It also shows that both PVA and TEA effectively reduced the viscosity and adsorbed to coal particles which confirms that the reduction in viscosity is directly related to the amount of dispersant adsorbed to coal particles. To be industrially

Table 3: CWS Samples at Variable Coal Loading.

Sample	Coal (g)	Water (g)	PVA (g)	TEA (g)	Xanthan gum (g)
CWS-30	30	98.7	0.47	1.144	0.25
CWS-40	40	98.7	0.47	1.144	0.25
CWS-50	50	98.7	0.47	1.144	0.25
CWS-60	60	98.7	0.47	1.144	0.25

Table 4: Data obtained from Power-law or Ostwald-de Wale model.

Sample	Power-law index	Consistency Factor (mPa.s ⁿ)
CWS-30	0.6774	315.355
CWS-40	0.5817	921.866
CWS-50	0.3958	4325.5
CWS-60	0.3386	7040.25

**Fig. 2: Viscosity vs Shear rate for CWS-30, CWS-40, CWS-50 and CWS-60.****Fig. 3: Data fitted on Power-law for different samples.**

relevant, the slurry stability of at least a few days is required, preferably longer. Hydrocolloids like XG added to increase the stability of suspensions and colloids by creating an additional flocculation network to keep particles separate. 0.25g of Xanthan gum did not affect the viscosity significantly but it increased the stability of slurry.

Power-law or Ostwald-De Wale Method

The Power-law rheological model (Equation (1)) was used to determine the flow behavior index and consistency coefficient by making a plot of \ln shear stress v/s \ln shear rate as shown in Figs. 3-7 for the sample

CWS 30 to 60%. Fig. 3 shows that the behavior of fluid is non-Newtonian as $n < 1$ at different coal loading and flow index decreases as shown in Table 4. This is due to the adsorption of PVA and TEA on coal particles which reduces the interparticle interaction. The bare coal particles are attractive due to van der Waals forces. This attractive interaction causes high viscosity at a low shear rate. As the shear rate increases the hydrodynamic forces applied to the system overwhelm the interparticle attractive forces, causing dissociation of aggregates which results in a lower viscosity. Figs. 4 to 7 shows that the behavior of slurry best fit by a power-law model with regression of 0.99.

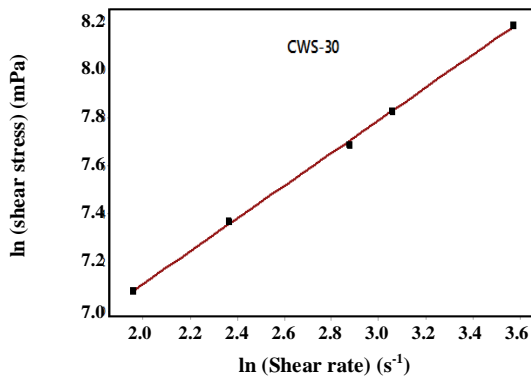


Fig. 4: Power-law model for CWS-30.

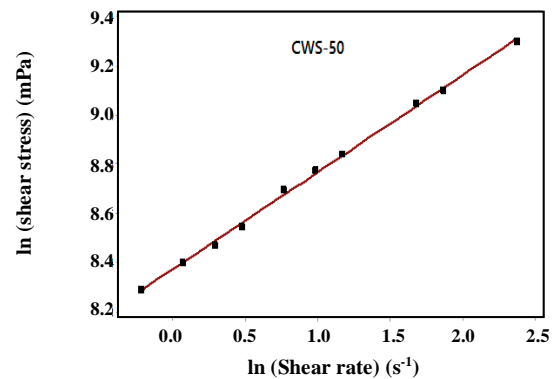


Fig. 6: Power-law model for CWS-50.

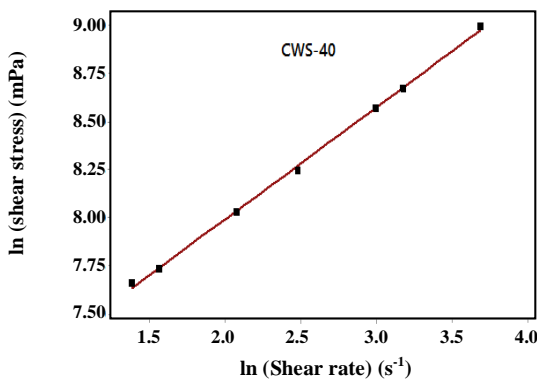


Fig. 5: Power-law model for CWS-40.

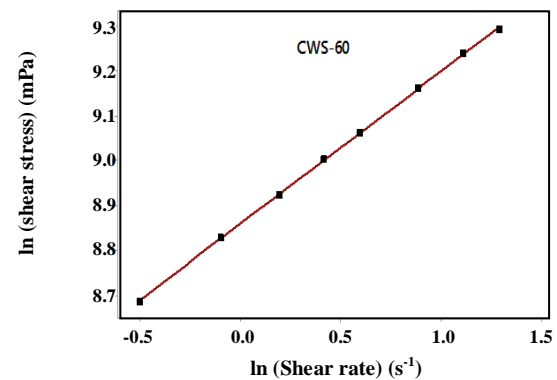


Fig. 7: Power-law model for CWS-60.

Casson fluid model

The shear thinning behavior of CWS samples also studied by the Casson model as shown in Figs. 8-12. In order to fit the Casson model the graph generated between $\tau^{0.5}$ and $\gamma^{0.5}$. Where y-intercept shows the square root of yield stress and the K_1 factor shows the secondary interaction forces of coal particles by which factor the apparent viscosity changes with respect to shear rate to the power half. Both factors increase as coal loading increases. The Casson yield stress and Casson plastic viscosity obtained from the graph as shown in Table 5.

Herschel bulkley model

The Herschel Bulkley model for CWS's 30 to 60% shown in Figs. 13-17. This model shows that for the flow of CWS requires some amount of shear stress, known as yield stress of the fluid. The Yield stress along with consistency factor increases as the coal loading increases. This is due to the amount of coal particles increases

in the solvent, which also increases the secondary forces. This will result in resistance to flow and the flow index shows how the viscosity is going to change with respect to the shear rate. For this study, $n < 1$ shows CWS is pseudo-plastic in nature, where the segregation of randomly arranged particles in the solvent occurs. If the amount of highly random particles is more, their apparent viscosity will be high and the segregation and the flow of particles in the direction of shear rate cause abrupt reduction of viscosity results in lower Power-law index this is the reason for reduction in flow index as the coal loading increases. The yield stress and plastic viscosity obtained from the graph for Herschel bulkley Model are shown in Table 6.

Comparison of Models

In this study, Power-law model, Casson model and Herschel Bulkley model were used to determine the best rheological model that accurately represents the rheology

Table 5: Data obtained from Casson Fluid Mode.

Sample	K_0 (mPa) ^{0.5}	K_1 (mPa.S) ^{0.5}
CWS-30	14.587	7.6141
CWS-40	26.071	10.198
CWS-50	49.643	17.633
CWS-60	54.26	25.579

Table 6: Data obtained from Herschel Bulkley Fluid Model.

Sample	Yield Stress (mPa)	Flow Index	Consistency Factor (mPa.s ⁿ)
CWS-30	450	0.8866	134.303
CWS-40	1000	0.806	372.44
CWS-50	2000	0.5851	2382.96
CWS-60	2500	0.4742	3969.51

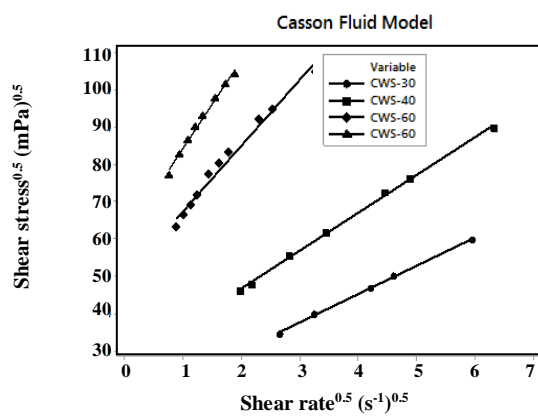


Fig. 8: Casson Fluid Model for CWS-30.

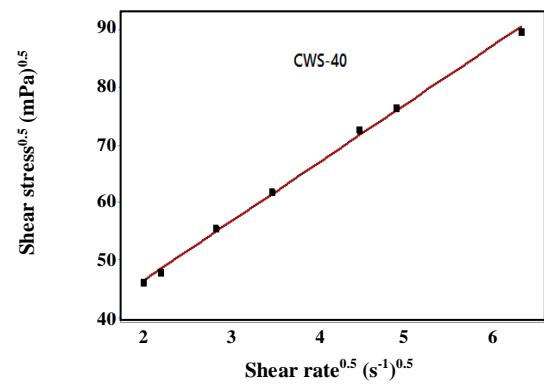


Fig. 10: Casson Fluid Model for CWS-40.

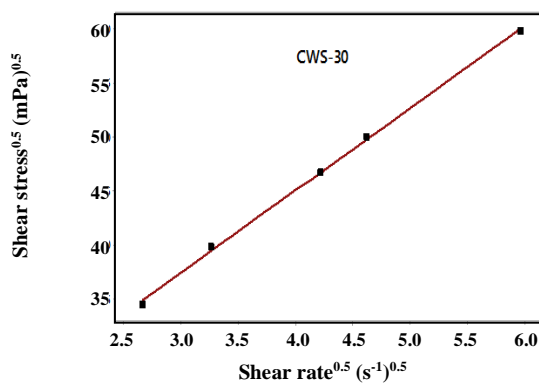


Fig. 9: Casson Fluid Model for CWS-30.

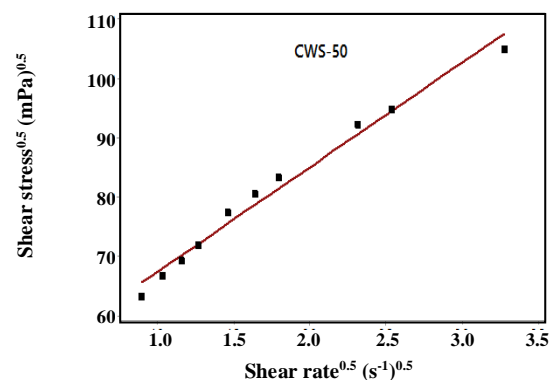


Fig. 11: Casson Fluid Model for CWS-50.

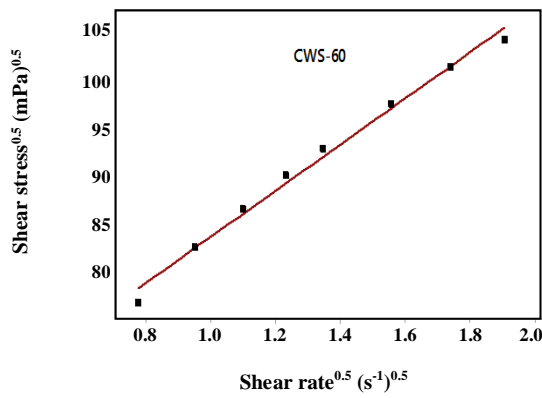


Fig. 12: Casson Fluid Model for CWS-60.

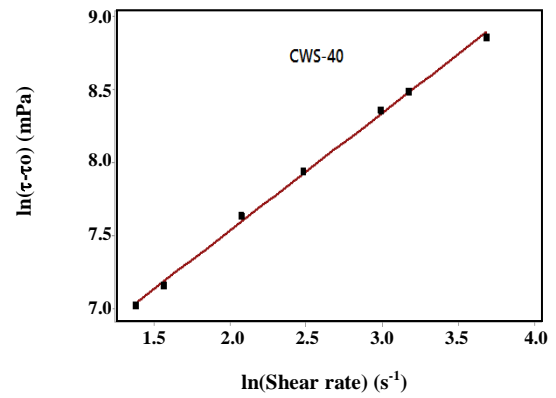


Fig. 15: Herschel Bulkely Model for CWS-40.

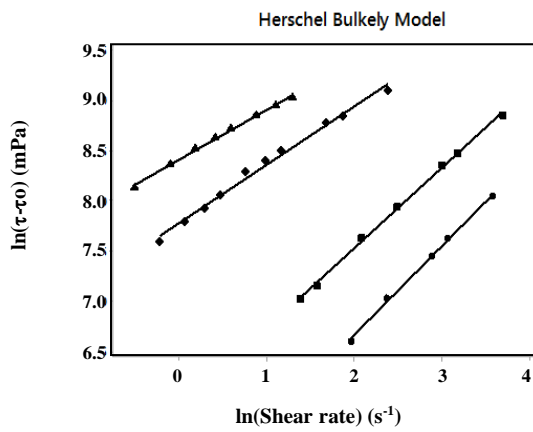


Fig. 13: Data fitted on Herschel Bulkely Fluid Model for different samples.

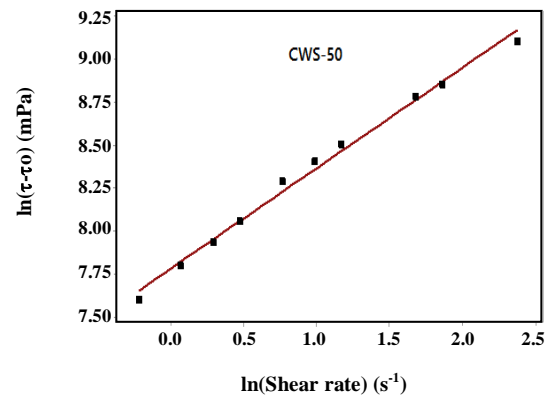


Fig. 16: Herschel Bulkely Model for CWS-50.

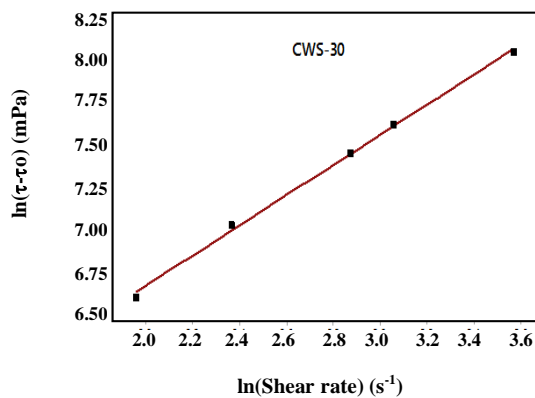


Fig. 14: Herschel Bulkely Model for CWS-30.

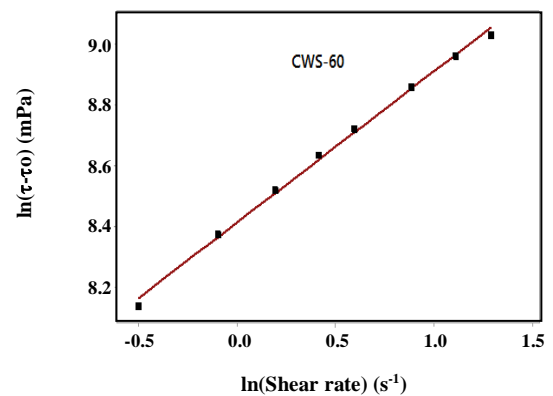


Fig. 17: Herschel Bulkely Model for CWS-60.

Table 7: Comparison of models based on R² Values.

Coal Loading	R ²		
	Power-law Model	Casson Model	Herschel Bulkley Model
CWS 30	0.9996	0.997	0.997
CWS 40	0.9989	0.993	0.9932
CWS 50	0.9983	0.974	0.9931
CWS 60	0.9974	0.957	0.976

of coal water slurry. The models were analysed on the basis of R² values as shown in Table 7. The analysis shows that the Power-law model accurately represent the flow behavior of slurry across the entire low and high shear rates condition at different coal loading. Herschel Bulkely model also predicts accurate flow behavior across the entire low to high coal loading, but higher accuracy is achieved with the Power-law Model. The Casson model the results does not predict the behavior accurately for high coal loadings, as the coal loading starts to increase, they tend to deviate from model.

CONCLUSIONS

The investigation was made to predict the rheological behavior of slurry accurately at different coal loading and the best model that can reliably characterize the slurry. The test results clearly indicate that PVA and TEA effectively reduced the viscosity at different coal loading and slurry exhibits Pseudo plastic behavior. Furthermore, it is evident from the study that Ostwald de Waele method accurately characterizes the slurry behavior over the range of 30 to 60% coal loading across the entire low and high shear rate conditions. The higher accuracy achieved by Power-law model as compared to Casson and Herschel Bulkley's model.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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REFERENCES

- [1] Lee S., "Alternative Fuels": CRC Press, (1996).
- [2] Fan Y., Hu H., Jin L., Zhu S., Zhang Q., *Static Stability and Rheological Behavior of Lignite Char–Water Mixture*, *Fuel*, **104**: 7-13 (2013).
- [3] Dmitrienko M.A., Legros J.C., Strizhak P.A., *Experimental Evaluation of Main Emissions During Coal Processing Waste Combustion*, *Environmental Pollution*, **233**: 299-305 (2018).
- [4] Dmitrienko M.A., Nyashina G.S., Strizhak P.A., *Major Gas Emissions from Combustion of Slurry Fuels Based on Coal, Coal Waste, and Coal Derivatives*, *Journal of Cleaner Production*, **177**: 284-301 (2018).
- [5] Dmitrienko M.A., Nyashina G.S., Strizhak P.A., *Environmental Indicators of the Combustion of Prospective Coal Water Slurry Containing Petrochemicals*, *Journal of Hazardous Materials*, **338**: 148-159 (2017).
- [6] Chakravarthy A., Kumar S., Mohapatra S., *Transportation Performance of Highly Concentrated Coal-Water Slurries Prepared from Indian Coals*, in *Applied Mechanics and Materials*, **592**: 869-873 (2014).
- [7] Mishra S., Senapati P., Panda D., *Rheological Behavior of Coal-Water Slurry*, *Energy Sources*, **24**: 159-167 (2002).
- [8] Boylu F., Dincer H., Ateşok G., *Effect of Coal Particle Size Distribution, Volume Fraction and Rank on the Rheology of Coal–Water Slurries*, *Fuel Processing Technology*, **85**: 241-250 (2004).
- [9] Buranasrisak P., Narasingha M.H., *Effects of Particle Size Distribution and Packing*, **3**, 31 (2012). *Characteristics on the Preparation of Highly-Loaded Coal-Water Slurry*, *International Journal of Chemical Engineering and Applications*, **3**: 31-35 (2012).

- [10] Harmadi E., Suwarmin S.M., Winardi S., [Effect of Particle Size Distribution on Rheology and Stability of High Concentration Coal-Water Mixture with Indonesian Low Rank Coal](#), *Jurnal Teknik Mesin*, **2**: 93-98 (2002).
- [11] Mosa E.S., Saleh A.-H.M., Taha T.A., El-Molla A.M., [Effect of Chemical Additives on Flow Characteristics of Coal Slurries](#), *Physicochemical Problems of Mineral Processing*, **42**: 107-118 (2008).
- [12] Pawlik M., [Polymeric Dispersants for Coal–Water Slurries](#), *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **266**: 82-90 (2005).
- [13] Yi F., Gopan A., Axelbaum R.L., [Characterization of Coal Water Slurry Prepared for PRB Coal](#), *燃料化学学报*, **42**: 1167-1171 (2014).
- [14] Singh A.K., Kumar S.G., [Rheological Investigation of Coal Water Slurries with and without Additive](#), MSc Thesis, Thapar University, Patiala, India (2012).
- [15] Ongsirimongkol N., Narasingha M., [Effects of Stabilizing Agents on Stability and Rheological Characteristics of the Highly-Loaded Coal-Water Slurry](#), *International Journal of Chemical Engineering and Applications*, **3**: 49- (2012).
- [16] Öztoprak A.F., ["Investigation Of The Rheological Properties of Çayirhan Coal-Water Mixtures"](#), Citeseer, (2006).
- [17] Chhabra R.P., Richardson J.F., ["Non-Newtonian Flow: Fundamentals and Engineering Applications"](#): Elsevier, (1999).
- [18] Herschel W.H., Bulkley R., [Konsistenzmessungen Von Gummi-Benzollösungen](#), *Colloid & Polymer Science*, **39**: 291-300 (1926).
- [19] Casson N., ["Rheology of Disperse Systems,"](#) In: *Proceedings of a Conference Organized by the British Society of Rheology*, (1957).
- [20] Briggs J.L., Steffe J.F., [Using Brookfield Data and the Mitschka Method to Evaluate Power-law Foods](#), *Journal of Texture Studies*, **28**: 517-522 (1997).
- [21] Miller S., Morrison J., Scaroni A., ["The Formulation and Combustion of Coal Water Slurry Fuels from Impounded Coal Fines,"](#) In: *19th International Technical Conference on Coal Utilization & Fuel Systems*, pp. 643-650 (1994).
- [22] Marchand D.J., Abrams A., Heiser B.R., Kim Y., Kim J., Kim S.H., [Rheological Modifiers for Petroleum Coke–Water Slurry](#), *Fuel Processing Technology*, **144**: 290-298 (2016).
- [23] Kozlov M., McCarthy T.J., [Adsorption of Poly \(vinyl alcohol\) from Water to a Hydrophobic Surface: Effects of Molecular Weight, Degree of Hydrolysis, Salt, and Temperature](#), *Langmuir*, **20**: 9170-9176 (2004).
- [24] Kozlov M., Quarmyne M., Chen W., McCarthy T.J., [Adsorption of Poly \(vinyl alcohol\) onto Hydrophobic Substrates. A General Approach for Hydrophilizing and Chemically Activating Surfaces,"](#) *Macromolecules*, **36**: 6054-6059 (2003).
- [25] Savitskii D., [The Effect of Water–Glycerol Mixtures on Rheological Properties of Coal Slurries](#), *Colloid Journal*, **78**: 109-114 (2016).
- [26] Tadros T., [Interparticle Interactions in Concentrated Suspensions and Their Bulk \(Rheological\) Properties](#), *Advances in Colloid and Interface Science*, **168**: 263-277 (2011).
- [27] Mukherjee A., Pisupati S.V., [Interparticle Interactions in Highly Concentrated Coal–Water Slurries and Their Effect on Slurry Viscosity](#), *Energy & Fuels*, **29**: 3675-3683 (2015).
- [28] Tadros T.F., ["Rheology of Dispersions: Principles and Applications"](#), John Wiley & Sons, (2011).
- [29] Xu Z., Chong L., Wang W., Chen Y., Tu Y.n., Zhang R., ["Coal Water Mixture Preparation Technology and Application in Replacing Oil to Generate Electricity"](#), In: *Power and Energy Engineering Conference, APPEEC 2009. Asia-Pacific*, pp. 1-5 (2009).
- [30] Usui H., Saeki T., Hayashi K., Tamura T., [Sedimentation Stability and Rheology of Coal Water Slurries](#), *Coal Preparation*, **18**: 201-214 (1997).