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Green strategies in formulating, stabilizing and pipeline transportation of coal water slurry in the framework of WATER-ENERGY NEXUS: A state ofthe art review

B.N.BISWAL, B.B.BHOI & D.DAS
Assistant Professor, Department of Basic Science and Humanities,
Nalanda Institute of Technology, Bhubaneswar, Odisha, India
E-mail: biswanathbiswal@thenalanda.com

Abstract

Advanced coal well treatment approaches and future developed technologies will make a greater contribution to addressing the challenges posed by the fuel crisis and the utilization of coal wells in an efficient, economical and clean manner. Coal slurry morphology and its stabilization has become an advanced research area in the field of coal processing technology. This review describes the role of key factors in stabilizing coal water sludge (CWS) with additives, the mechanism of interaction between the additives used and coal particles, and the flow behavior of CWS. Various factors influencing the modification of coal interfacial properties have been discussed, including adsorptive surfactants or dispersants, coal particle size distribution, and exposure to advanced techniques such as ultrasound, microwave radiation, and temperature. It has been observed that different techniques such as green natural surfactants alone or mixed with synthetic surfactants in the preparation of slurries can reduce harmful gas emissions during combustion. Important results include the problem of agglomeration and significant coal particle sedimentation, the existence of van der Waals attraction between coal particles in highly concentrated coal water slurry (HCCWS), minimization of slurry viscosity during pipeline transport. Proven by Driving flow behavior and behavior of HCCWS like liquid fuels in combustion and economics has been extensively discussed and summarized.

Abbreviations

CWS	coal water slurry	TG	Thermogravimetry
CFS	Coal fuel slurry	^{1}H NMR	proton nuclear magnetic resonance
HCWS	high concentration coal water slurry	HAP	humic acid-based polycarboxylic-type
CMC	critical micellar concentration	PPA	Polyoxyethylene Polycarboxylic Acid ether
PSD	particle size distribution	SMF	Sulfonated Melamine-Formaldehyde resin
SDBS	sodium dodecyl benzene sulfonate	NaSS	sodium styrene-sulfonate
DDAB	di-docyl ammonium bromide	CFS	candanol formaldehyade sulfonate
SDS	sodium dodecyl sulfonate	SAF	sulphonated acetone–formaldehyde resin
CTAB	cetyl trimethyl ammonium bromide	HDBAC	benzyl hexadecyl dimethyl ammonium chloride
FDN	naphthalene sulfonate formaldehyde condensate	OTAC	octadearyl dimethyl ammonium chloride
NSF	naphthalene sulfonate-formaldehyde	CTAC	cetyl trimethyl ammonium chloride
AMPS	2-acrylamido-2-methylpropanesulfonic acidSTPP	PC	polycarboxylic acid
	sodium tripolyphsphate		
FTIR	Fourier transform infrared		

*

HA-g-PSSNa	humic acid-graft-poly (sodium styrene sulfonate)
BTU	British thermal unit
□	shear stress
□	viscosity coefficient
n	flow index
K	consistency of fluid
$□_□$	Plastic viscosity
$□_o$	Yield stress
V_A	Van der Waals attractive force
V_R	repulsive force
V_S	solvent potential energy
A	fitting parameter
R	Universal gas constant
□	apparent viscosity at a particular shear rate
T	temperature in Kelvin
E	activation energy
q_e	Saturated amount of adsorption (mg/g)
K	Adsorption parameter
C_e	Equilibrium concentration (mg/L)

1. Introduction

Coal is extensively used as a fossil fuel in thermal power plants to generate energy. As stated in earlier reports [1] countries like India have almost 60% of their thermal power plants primarily dependent on coal. Notwithstanding its economic importance, there are serious environ- mental concerns due to the losses due to the coal dusts at the mine site and the coal industries and concern due to the environmental pol- lution caused by the coal fine particles. Generally the particulate formof coal dust often mixes in the air as flue gas consequently causing air pollution. Therefore, environmental issues related to soil, air and water pollution escalate by coal dust particles can be minimized by adopting clean technology [2]. Overall beneficiation and up gradation of coal particles vis-à-vis minimization of pollution caused by coal dust can be well handled by employing the process of pipeline transportation of coal from the sites to the desired location after making suitable coal water slurry (CWS). The slurry being resulted out of coal needs to be well sta- bilized prior to its pipe line flow and in consequences of which the cost incurred during transportation of CWS can be significantly reduced. In this way the development of a promising, clean, economical and sustain- able technology for transportation of CWS (with less supplement of wa- ter on making slurry) having a high pumping ability is warranted [3,4]. Thus, analyzing the rheology of coal ash slurry is important for chem- ical engineers to understand the details of its viscosity and yield stress during pipeline transportation. To ascertain high throughput in pipeline transport and high slurry transportation yield, the role of surfactants is noticeably crucial in addition to other factors like, shape of particles, particle size distribution, solid concentration in slurry and slurry viscos- ity [5,6] that affect the flow behavior of fly ash slurry. With suitable dose of surfactant supplement in slurry, its viscosity and shear stress couldbe decreased. As a result, the possibilities of high percentage of solid concentration in the transported slurry could be enhanced significantly [7].

The interaction of additives with the slurry particle impacts the flow behavior of slurry, and thus, surfactant selection is critically important. Though, commercial additives are quite common in slurry stabilization, green strategies like the use of natural surfactant appears to be promis- ing with numerous advantages. The effect of shear stress and strain, and interaction mechanism of additive with the slurry towards the reduc- tion of viscosity, slurry transport behavior and the stabilization of vari- ous CWS systems is extensively reviewed and reported [8]. This review covers the adopted green processing strategies, and its futuristic scopein CWS stabilization. The key associated environmental issues could be addressed through this while the huge waste coal ash could be managed in promising and cleaner means.

Coal water slurry (CWS)

Slurry is the blending of solid and liquid in an approximately equiva- lent ratio, its physical characteristics being dependent on factors like the particle size, solid concentration, temperature, turbulence level and vis- cosity of the carrier. There is a famine in crude oil owing to its increased consumption, ever-increasing cost, paucity of supply and dwindling re- serve which has promoted increasing interest and research related to the more efficient and smarter use of coal. Coal is an abundantly available resource at a rational cost. Thus, coal slurry could be an alternative to petroleum oil as a liquid fuel. Such slurry could be of different types based on the types of liquid as vehicle, *viz*., CWS, coal-oil-water slurry, coal-oil slurry, etc. From economics point of view, researchers consider CWS as of great potential to generate power considering its availability and the cost: benefit ratio. It is a fuel oil substitute in boilers for en- ergy. It is user-friendly also owing to its low inflammability and high combustion efficiency.

Historical development of coal water slurry (CWS)

Global crude oil crisis became obvious towards the end of the 70 s. Having scarce crude oil, nations import crude oil from Saudi Arabia, Iran, Venezuela, Canada, etc. India's import is up to 80%, spending huge revenue. However, it has large industrially-utilizable coal reserves. To-wards the end of the 80 s, scientific investigations and technological interventions validated the use of coal as a substitute for crude oil. Withan estimated 589 million ton coal reserve in India, coal caters to approx- imately 51% of the energy needs.

Primarily, solid coal is used in combustion and electricity genera- tion [9,10]. Prior to combustion for electricity generation, it is usually crushed to fine powder (pulverized coal or coal dust) which improves its burning efficiency. The heat thus generated converts the boiler water to steam which in turn spins the turbine to produce thermoelectricity.

As coal dust suspends in air causing pulmonary illness among work- ers when inhaled in excess, the pulverized (powder or dust) coal is a health concern. Further, it is unsafe to store as it is a potential explo- sive. To address these issues, coal-water mix is a wiser alternative. Coal liquefaction and gasification is economical compared to its pulverized counterpart. It behaves like a liquid fuel in combustion as a fuel [11]. Another advantage of it is that it could be transported in pipeline with- out the risk of explosion.

The US, Germany and the USSR are pioneers in CWS since 1960. In 1980, the US emphasized on standardizing the technology for easy han-dling and transport of CWS with matching physicochemical propertiesto the then existing boilers and equipments. As the crude oil price eased, the interest in this waned. Energy-dense bituminous coal was the early endeavor for CWS technology. The use of low rank coal (LRC) like the naturally pulverized coal with water without chemical additives for the purpose was uneconomical [12]. Introducing chemical additives made the LRC efficient [13].

Particle size distribution of the high solid concentration and chem-ical additives cover the particle interface, reduce the viscosity and in- crease its stability to match with crude oil. This way, it could be pumped, and specially designed nozzle could atomize it in a preheated environ- ment making it suitable for boiler or furnace combustion [14]. CWS should have maximum coal loading capacity and transportation stabil-ity to achieve ideal fuel property and enhanced fuel efficiency. It should have good rheological behavior during transportation that would facili- tate slurry atomization. The viscosity of such mixture should ideally be about 1000cp at 100 rpm [15].

Classification of coal

Buried plant materials transform physically, chemically and biologi- cally under high geological temperature and pressure to form coal. This metamorphosis leading to various degree of coalification from peat to anthracites through lignite and bituminous determines its quality. The quality depends on the volatilizable matter and moisture contents in the coal. For instance, peat contains the lowest carbon, and anthracite contains the highest. Various forms of coals with special traits are:

Peat: Considered as a coal predecessor, it is used as a fuel in countries like Ireland and Finland. It could also soak up oil spills.

Lignite: Quality-wise, it is at the bottom of the coal category. Mainly used in electricity generation, it is high on moisture, contains about 25–35% carbon and has 4000–8300 BTU per pound calorific value.

Sub-bituminous coal: Used as a fuel in thermoelectricity genera- tion, it contains 35–45% carbon and 8300–13,000 BTU per pound heat- ing value.

Bituminous: It is a high quality coal formed when lignite is exposed to additional heat and pressure. It has 45–86% carbon and is mostly used for electricity generation in iron and steel industries. It has a heating value of 11,000–15,500 BTU per pound, 3–4times more than lignite.

Steam coal: Quality-wise, it is ranked between bituminous and an- thracite. Used as a fuel in steam locomotive, it is also used for domestic purpose.

Anthracite: Formed under very high geological temperature and pressure it is categorized as a high quality coal. It is ranked high for its fuel properties. Its glossy surface gives it a metallic look. With a carbon content of about 86–97%, it has 15,000 BTU per pound heat capacity.

Bingham plastic model follows the equation:

$$\tau = \tau_0 + \eta\left(\frac{du}{dy}\right) \quad (3)$$

where, τ = shear stress, η = Plastic viscosity, τ_o = Yield stress and (du/dy) = shear rate

Graphite: Though ranked high on coal properties, it is difficult to ignite. Thus, it is not used as a fuel. The tip of a pencil is made of graphite and its powder form is used as a lubricant.

Coal is further classified into three categories based on its ash con- tent, as high ash (more than 30%), medium ash (15–30%) and low ash (below 15%) coals. Fuel efficiency of CWS demands high coal concentra- tion. It should also maintain minimal viscosity to be suitable for pipeline transport.

Viscosity of coal water slurry (CWS)

The flow behavior and suspension viscosity of CWS are critical for pipeline transport. Viscosity rises largely due to the presence of Van der Waal forces of attraction of coal particles. This should be minimizedfor ease of flow of the slurry for carriage through pipeline. The viscos-ity varies inversely with the shear rate. Understanding the variation of viscosity with the shear rate is therefore highly essential. For its suitability as a fuel, the viscosity of CWS should be within 1000 mPa-s. While adding coal to water, the viscosity of the slurry invariably increases compared to that of the water alone. Coal particles make coal-water solution thicker and influence velocity distribution in a laminar flow, which in turn influences the viscosity. The suspension viscosity is the laminar flow parameter which is directly related to the velocity gradient and shear stress. Depending on the response of the shear stress with the shearing rate, fluids are described as Newtonian or non-Newtonian.

In a laminar flow, the line passes through as expressed in the below equation.

$$\eta = \frac{\tau}{\frac{du}{dy}} \quad (1)$$

where, τ = shear stress, η = coefficient of viscosity and (du/dy) = shear rate

Pseudo-plastic fluid obeys the power law is a non-Newtonian fluid flow following the equation:

$$\tau = K\left(\frac{du}{dy}\right)^n, n < 1.0 \quad (2)$$

where, n = flow index, K = consistency of fluid, τ = shear stress, $\frac{du}{dy}$ = shear rate

For a more viscous fluid, the 'K' value is more. Dilatant fluids obey the power law also a non-Newtonian fluid flow with a flow index n>1.0.

Similarly, Bingham plastic fluids and Herschel-Bulkley or visco-elastic fluid are non-Newtonian fluids with some value of yield stress.

In Herschel-Bulkley model follows the equation:

$$\tau - \tau_o = K\left(\frac{du}{dy}\right)^n \quad (4)$$

where, τ_o = yield stress, τ = shear stress, K = consistency of fluid, (du/dy) = shear rate and n = flow index.

DLVO theory of colloidal stability: Stability of CWS

The coal content in the slurry should be as high as possible for the CWS to be economical. But, an increased cohesive force among the coal particles in concentrated slurry increases its viscosity. Viscosity increases with coal loading that would adversely affect the ease of transport through pipeline [16]. Hence, tradeoffs between optimum viscosity and stability in concentrated slurry are necessary.

Particles collide with each other during Brownian movement. Due to the strong particle-particle hydrophobic interaction, particles conglomerate, flocculate and settle down, thereby destabilizing the slurry. By masking the hydrophobicity of coal or modifying its surface, the hydrophilicity of the coal-water interaction could be increased [17]. In general, factors that lead to mutual repulsion between the particles help in the formation of a well-dispersed suspension. Mutual repulsion is measured by a theory called DLVO theory, the basis of the slurry stabilization.

DLVO theory was developed by Derjaguin, Landau, Verwey and Overbeek [18,19]. It suggests that the total potential energy V_T of a particle which is the sum of attractive contributions (V_A), repulsive contributions (V_R) and solvent potential energy (V_S) determine the stability of a particle in slurry. V_S has the least contribution to the total potential energy, but V_A and V_R largely determine the stability of the colloid. Two forces arise among particles due to Brownian motion, the van der Waals attractive force (V_A) and the electrical double layer repulsive force (V_R).

DLVO theory says that the particle repulsive force creates an energy barrier preventing any two particles to approach each other and adhere, during Brownian motion. Coagulation is possible if the attractive force among the particle pulls them into contact for strong adherence to occur. Repulsion must dominate over flocculation to maintain the stability in a colloidal system.

If weaker and reversible adhesion occurs in particle, a secondary minimum is formed. These are weak flocs that can't be broken by the Brownian motion but could dissociate by external forces like mechanical force such as agitation. High concentration is an example, where this situation may be noticed.

The two fundamental mechanisms that affect the stability of dispersion are (Fig.1.)

Steric repulsion: It occurs when a dispersing agent adsorb on the particle, thickens the coating of dispersing agent at the particle interface creating steric repulsions that minimize the vander Waals forces of interaction among the particles. This way it prevents particle-particle contact, prevents particle adhesion, and check flocculation.

Electrostatic stabilization: Distribution of charged species in the system leads to the repulsion between particles thereby stabilizes the system. It is referred as electrostatic stabilization. The particle must be sufficiently wet by the solvent. It prevents particle-particle interaction and hence the dispersion is stabilized.

2. Factors affecting the stability of CWS

The factors that are primarily responsible and directly or indirectly affecting the stability of high concentration CWS are discussed under:

- Adsorption of dispersant

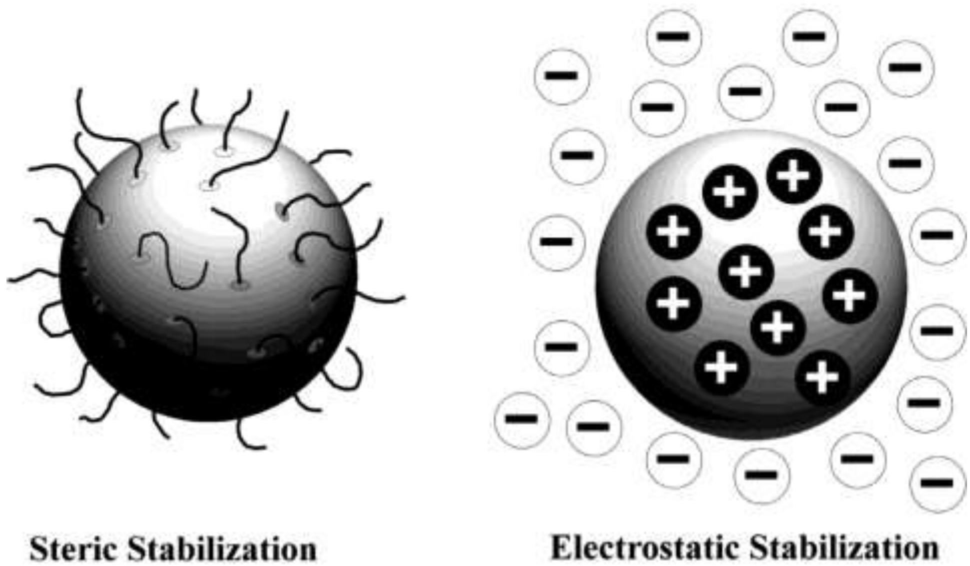


Fig. 1. Schematical presentation of two fundamentals stabilization.

- Particle size and its distribution
- Effect of Microwave treatment
- Exposure to ultrasonic radiation
- Temperature of the suspension

Adsorption of dispersant (like surfactants, polymers, etc.)

Synthetic or commercial dispersant

Surfactant molecules are amphiphilic in nature consisting of a long-chain hydrophobic tail and a hydrophilic head. It has the unique property to reduce the surface tension of water. Surfactant molecule adsorbs at the air-water interface by orienting its hydrophilic head towards water and hydrophobic tail towards air, thus reducing the liquid-air interfacial tension [20]. Depending on the head of the hydrophilic charged group, a surfactant may be cationic or anionic [21]. Above a particular concentration (critical micelle concentration; CMC) when air-water interface is saturated with complete formation of a monolayer, the residual surfactant molecules form a bulk (cluster like structure) called micelle. Thus, above the CMC there is no further reduction in the liquid-air surface.

Using an appropriate dispersant in an appropriate quantity is therefore necessary to obtain a suitable CWS. Investigation on the adsorption pattern of a dispersant is critical as it decides the rheological behavior of CWS. The important role of surfactant can be summarized as follows:

- Modifying the surface charge on the coal particles
- Controlling the relative hydrophilic/hydrophobic character of coal
- Forming a 3-D structure that prevents coagulation in CWS

A surfactant that satisfies the following criteria can be used as a dispersing agent:

- It should be water soluble, non-foaming and effective at low concentration.
- It should be compatible with the stabilizer.
- It should have a structure compatible with flat adsorption on coal surface.

The rheology of CWS depends upon the type of coal molecular weight, molecular structure, length of the side chain, ratio of hydrophobic to hydrophilic groups, the nature and quantity of the polymer, etc. [22]. With an increase in the molecular weight of dispersant, the concentration of the ionized functional groups (carboxylic and sulfonic, etc.) increases which protruded to the outer side of water medium while increasing the strength of the electrical double-layer repulsion and repulsion between the coal particles. Hence, the apparent viscosity decreases with an increase in the molecular weight. With an increase in the PEO side chain length in molecular structure of dispersant, the apparent vis- cosity decreases since the electrically neutral PEO side chain protrudes outside into the bulk solution, affecting the steric repulsion between the coal particles. It has a major role in viscosity reduction. When NSF is used as a dispersing agent, only an electrostatic repulsion is experi- enced due to flat adsorption of NSF to the coal surface. However, both electrostatic and steric repulsion may be experienced when a copolymer is used as dispersant [22].

The alkyl groups present on the surfactant adsorb onto the hydropho-bic site of the coal, resulting in a partial negative charge on the surface which attracts counter cations to the interface to form an electrical dou- ble layer [23]. Such electrical double layer creates steric repulsion while approaching towards each other, thus inhibiting the coal particle con- glomeration. So, with an increase in proportion of surfactant; the ap- parent viscosity sharply decreases all of a sudden, reaching a minimum.CWS viscosity remains constant in a fairly broad range of surfactant loading though [24].

Nonionic surfactant can also be used as a dispersing agent to stabi- lize the CWS. The mechanism of stabilization in this case is quite dif- ferent from that of anionic surfactant [23]. The stabilization of CWS by a nonionic surfactant is explained in following ways. The surfactant may adsorb to the coal surface in two ways. In the first plausible mech- anism, the hydrophilic site of the surfactant may adsorb on to the hy- drophilic site of the coal surface orienting the hydrophobic sites of the surfactant molecules towards the aqueous phase of CWS. This may de- crease the viscosity of CWS. In the second plausible mechanism, the hydrophobic sites of the surfactant may adsorb on to the hydrophobic coal surface, orienting the hydrophilic site towards the aqueous phase. In this, due to the formation of hydrogen bonding with the polyethoxy- lene chain with water molecule, the amount of water at the surface ofthe particle increases, thereby decreasing the viscosity. Also, similar is
the non-ionic dispersant poly-oxyethylene sorbitan monooleate on Turk- ish lignite. The carboxylic functional group in the hydrophilic area of the coal formed a stable inter-polymer complex with poly- oxyethylene chain. An inter-polymer complex is formed between the hydroxyl group of carboxyl and oxygen atom of the poly-oxyethylene chain through hy- drogen bonding [25]. Same steric stabilization principle was applied to explain the interaction of Triton-X on coal surface [26]. Triton X- 405 formed spherical micelles with the -OH radicals on the outsides, attached to the surface. Measurement of zeta potential showed that the suspension stabilized by non-ionic and ionic surfactant behaved differ-

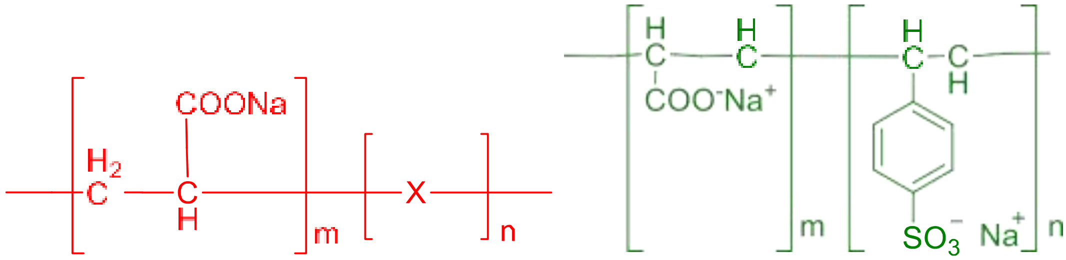


Fig. 2. Schematical presentation of molecular structure of: a) sodium polyacrylate copolymer with various co monomers) sodium styrene-sulfonate (NaSS) and b) sodium acrylate copolymer.

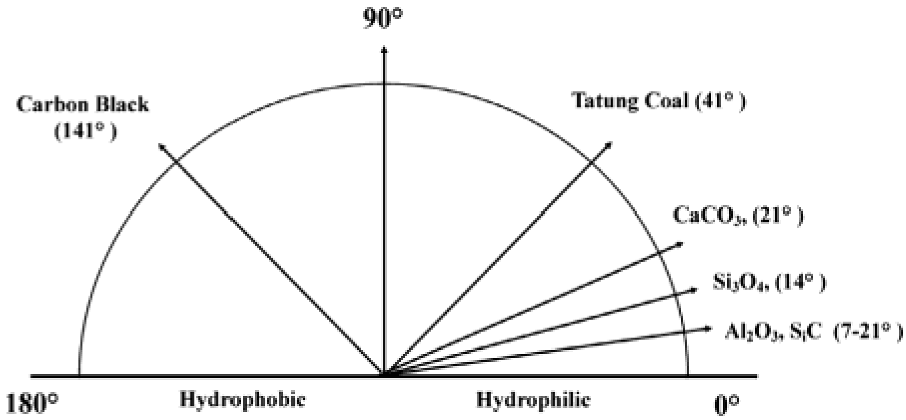


Fig. 3. Schematical presentation of contact angles of powder of different substance with water.

ently. The non-ionic poly-ether repellent adsorbed on the coal surface formed a monolayer wherein each surfactant molecule attached to the coal surface at more than one site. The adsorbed dispersant stabilized the colloidal system by shifting the zeta shear plane away from the coal surface. According to Zhu et al. steric repulsion among coal particles has a major contribution towards stabilization of CWS. Karatepe et al. postulated that surfactant acts as a coat on the surface of coal and according to Aktaş and Woodburn et al., a monolayer of surfactant is formed on each coal surface along with the spherical micelle in the bulk solution.

Electrostatic stabilization of CWS can be explained by taking examples of ionic surfactants SDS and CTAB. These adsorb on the coal surface through their hydrophobic groups while the hydrophilic group is oriented towards the aqueous phase. The highest decrease in viscosity was observed by using CTAB as a dispersant. This may be explained by considering electrostatic interaction of cationic dispersant CTAB with the negatively charged functional groups on the coal surface which increases the interaction between the coal and the surfactant. Both hydrophobic and electrostatic interactions occur with an increased CTAB concentration [27]. Dyna flow and NSF surfactants, containing naphthalene ring, are hydrophobic in nature. So, the affinity towards coal surface which contains hydrophobic polycyclic naphthalene ring is high.

Flat adsorption of naphthalene ring occurs on coal surface producing electrostatic repulsion. Besides electrostatic repulsion effect, steric hinderance of Dyna flow is also there. Dyna flow therefore is a better dispersing agent than NSF [28].

Yavuz and Küçükbayrak investigated the interaction of polymeric anionic surfactants Pellupur B69 and Texapon N25 on Turkish lignite CWS [29] . Pellupur B69 is a formaldehyde condensate sodium salt of naphthalenesulfonic acid (NSF) and Texapon N25 is sodium lauryl ether sulfate used as a wetting agent. The investigation was on the factors like oxidation, demineralization, mixing time, PSD, slurry and dispersant concentration that influenced the adsorption pattern on coal surface thereby changing the rheological characteristics of CWS. They reported that, upon oxidation, the hydrophilicity of coal increased and the adsorbing power decreased owing to the formation of acidic functional group in the activated site of aromatic ring. Additionally, adsorption ofthe dispersant became less in demineralized coal. There was sharp decline in the dispersant adsorption in de-mineralized lignite with a higher surface area, compared to that of the native. Hence, dispersant adsorption behavior may be attributed to the difference in the surface area and the minerals content. The rheological behavior of CWS was investigated taking Tatung coal powder with dispersant, sodium aromatic sulfonate, synthesizing anionic copolymers with various hydrophilic and hydrophobic groups or different molecular weights from 11 kinds of monomers to determine the optimum molecular structure. The molecular structure of different polymers is as below (Fig. 2a and Fig. 2b).

From contact angle measurement as depicted in Fig. 3., it is found that the contact angle of Tatung coal was 41° This is lower compared to the hydrophobic carbon black (141°) and higher compared to the hydrophilic powders like alumina and calcium carbonate (7–21°). Thus, it confirms that coal particle surface consists of both hydrophilic andhydrophobic sites [30].

Fig. 4. shows the hydrophobic adsorption mechanism between multi-ring part of the hydrophobic coal surface and aromatic groups in sodium salt of aromatic structure. Thus, electrostatic force repulsion occurs between the hydrophilic sulfonate groups of the dispersant with the hydrophilic functional groups of coal surface.

So it can be stated that, in addition to the nature of dispersant, min-eral content of coal [29] and hydrophilic character of coal has a signif- icant effect on the stability of CWS.

Two water-soluble polymers SAF and NSF were used to formulate highly concentrated CWS from four Chinese coal variants for industrial application [31]. The structure of SAF and FDN are given in Fig. 5a andFig. 5b.

SAF resin is a high molecular weight and water soluble polymer containing hydroxyl, carbonyl and sulfonic groups, and a large number of hydrophilic and hydrophobic sites. SAF has higher molecular weight and shows better stability and fluidity than that of FDN. It has been investigated that shear-thinning behavior was in the CWSs prepared from above four kinds of Chinese coals at lower dosage NSF when SAF

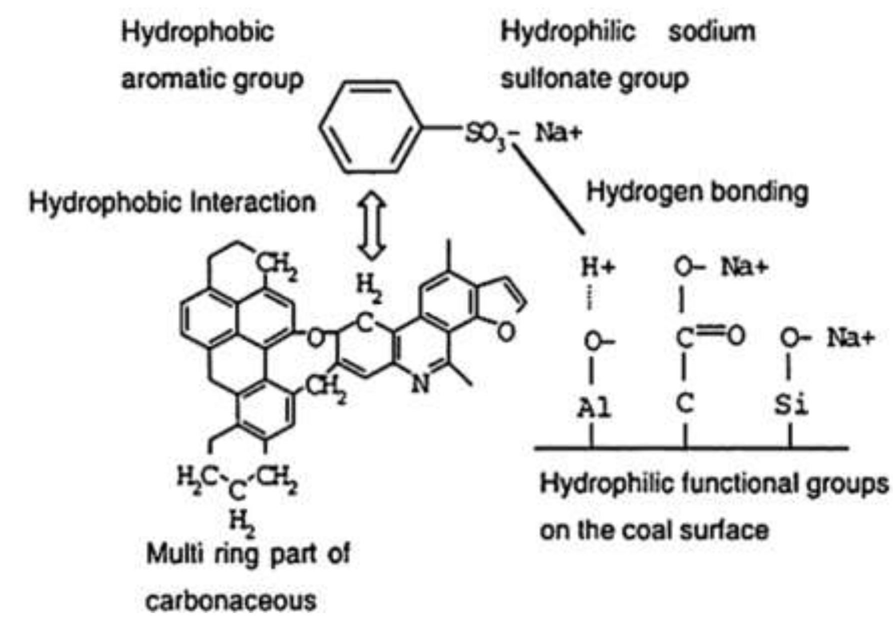


Fig. 4. Schematic presentation of the ion-bonding force and hydrophobic interaction between the coal surface and polymer dispersant.

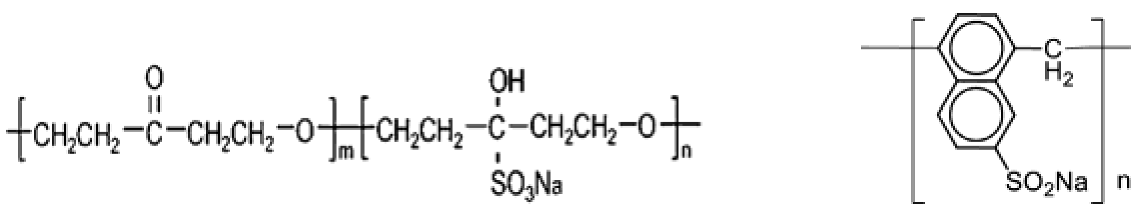
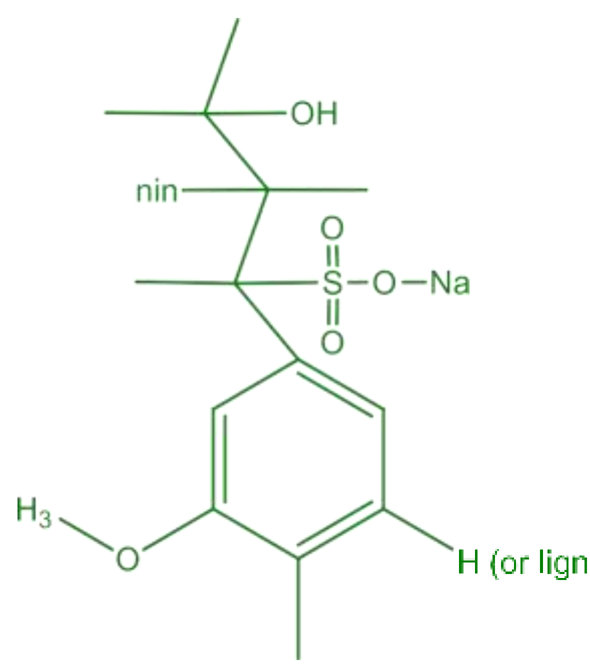


Fig. 5. Schematical presentation molecular structure of: a): SAF; b) NSF.

was used a dispersant. It showed Newtonian behavior at high shear that could be exactly described by the Herschel–Bulkley model. Another type of SAF resin was synthesized and evaluated as a suitable dispersant to stabilize CWS using techniques like measuring the surface tension, Infrared spectrum analysis and the inherent viscosity [32]. CWS with 65% coal concentration by using 0.7–0.8% SAF resin as dispersant was achieved. Tiwari et al. [33] formulated and characterized CWS using two additives, 0.8% wt/wt naphthalene (P) and 0.9% wt/wt naphthalene-toluene based additives (R) on two low-rank Indian coals considering the parameters like additives concentration, additive package, coal particle size distribution, volume fraction of coal, and method for CWS formulation. The static stability of CWS for the additives P and R was found to be 21 and 20 days, respectively. The rheological characteristics CWS also depends upon the relationship between bound water content of coal with dispersants like Sodium lignosulphonate (SL) and FDN [34]. Volatilization cut-off points of free water and bound water in CWS was discriminated by using thermo-gravimetric (TG) analysis. The viscosity of CWS and its rheological characteristic were affected by the molecular weight of the additives (Fig. 6.) [35]. In this connection, four fractions were prepared by changing the cut off molecular weight of the membrane, *i.e.*, Fraction 1 of <5000, 2 of 5000–10,000 taken, 3 of 10,000–50,000, and Fraction 4 of >50,000.

The content of hydrophilic group decreased with increasing molecular weight. L type adsorption curve was obtained for 10,000–50,000 fractions indicating its more adsorptive capacity. Zeta potential of this fraction reached to −52 mV.

Dispersants adsorption on coal surface caused an increase in the quantity of surface charge and the amount of hydration water content. It has been investigated that addition of dispersant decreased the bound



water content sharply in high-rank coal, whereas the bound water contents decreased normally in low-rank coal CWS. It may be explained

Fig. 6. Schematical presentation molecular structure of Sodium lignosulfonate.

based on the fact that water molecules are weakly bound on the surfaceof high-rank coal with more hydrophobic zones [35].

The combined effect of dispersing agent and stabilizer on rheological characteristics of CWS of Turkish bituminous coal was studied taking a

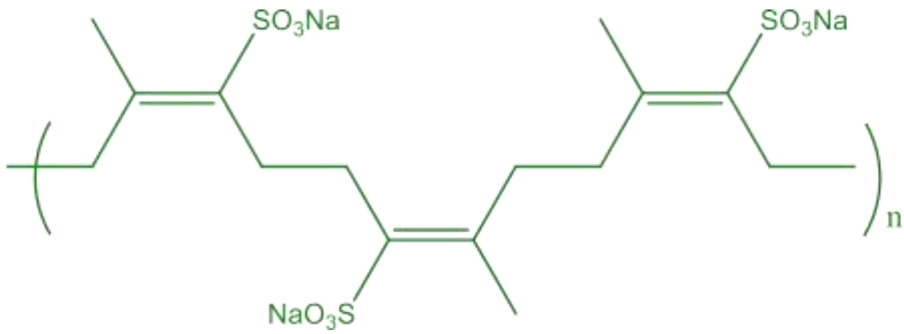


Fig. 7. Schematical presentation molecular structure of Dynaflow-K.

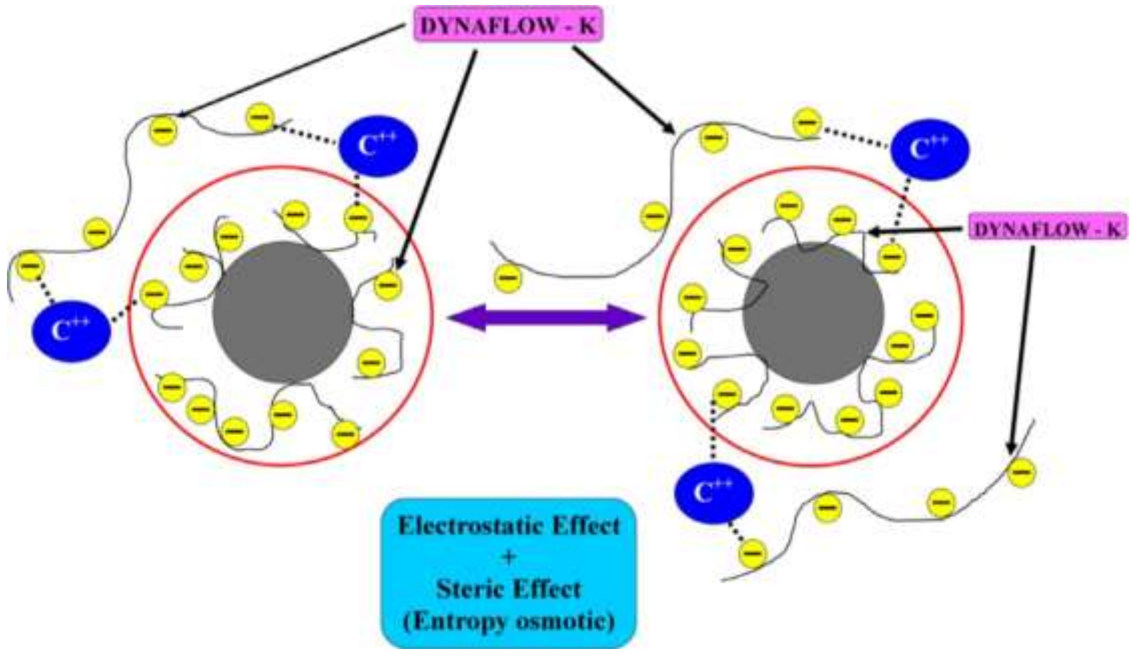


Fig. 8. Mechanism of dispersion of Dynaflow-K on coal surface [36].

mixture of Dyna flow-K (Fig. 7.) and NSF condensate as a flow improver and carboxy-methyl-cellulose (CMC) as the stabilizer. CMC had no significant effect on the viscosity of CWS in the presence of Dyna flow but had significant effect in presence of NSF.

The naphthalene ring of NSF has high affinity towards the multi-ring carbonaceous hydrophobic coal surface. Therefore, it might be adsorbed flat on the surface. Hence, coal particles experience only the electrostatic repulsion. Dyna flow adsorbed on the surface in such a manner that a loop or tail would protrude to the bulk (Fig. 8). Hence, both steric hindrance effect and electrostatic repulsion could be expected between the coal particles when Dyna flow was used as dispersant.

The effect of blended high ash coal in presence of commercial dispersant Naphthalene sulfuric acid-formaldehyde condensate was studied for preparation of a stable CWS [37]. It was postulated that with decreased ash content, oxygen to carbon ratio, the number of polar functional groups in the slurry increased and slurry ability is improved. The packing efficiency varied with the grinding ability which helped prepare highly loaded CWS. The Zeta potential was favorable at fixed dispersant concentration to decrease the viscosity of CWS and to improve rheological properties. Adding high-rank coal in CWS further reduced the energy and oxygen consumption. They concluded that coal blending reduced the attentiveness of oxygen functional groups and anionic additives increased the surface adsorption of coal effectively, thereby improving the slurry ability. Influence of chemical additive on the rheological behavior of CWS was studied taking three dispersants, sulphonic acid, sodium tripoly phosphate and sodium carbonate, in the 0.5–1.5% wt range. In addition to it, two stabilizers, sodium salt of carboxymethyl cellulose (Na-CMC) and xanthan gum, were introduced in 0.5–0.25% wt range. Among these, sulphonic acid and Na-CMC combination was the most suitable to prepare CWS [38]. The effect of dispersant pre- pared from black liquor by sulphonation process on bituminous coal CWS was reported by Zhou et al. It was observed that the sulfonic group content could be increased by increasing the concentration of sulfonat- ing agent and formaldehyde [39]. Compared to naphthalene, dispersant black liquor had better dispersability; change in molecular configura- tion gave excellent dispersing effect of the black liquor in CWS. Ampho- teric dispersant synthesized from methyl acrylic acid (MAA), sodium al- kali sulfonate (SAS) and methacryloxyethyl trimethyl ammonium chlo- ride (DMC) at 0.5 wt.% was employed to prepare CWS [40]. It was ob- served that when the anionic: cationic monomer ratio was 3:1; the CWS had the best rheological behavior with lowest apparent viscosity. Wang et al. used municipal sewage sludge usually containing water and nox- ious substances as a co-dispersant in CWS [41]. Five coal-sludge slurry (LJ, QJ, NS, pH, and BH) were considered and parameters like stability, rheology, shear rate, temperature etc. were measured. Sewage sludge and additive mixed coal behaved pseudo-plastically. The maximum solid loading dropped by 9.5–12.5% by varying the water content from 0 to 15%. LJ and NS, with lower viscosity and solids content, had good sta- bility. Organic alcoholic chemicals, *viz*., ethanol, methanol, 2-propanol, pentanol, hexanol and octanol at 1–10% wt. concentration can act as

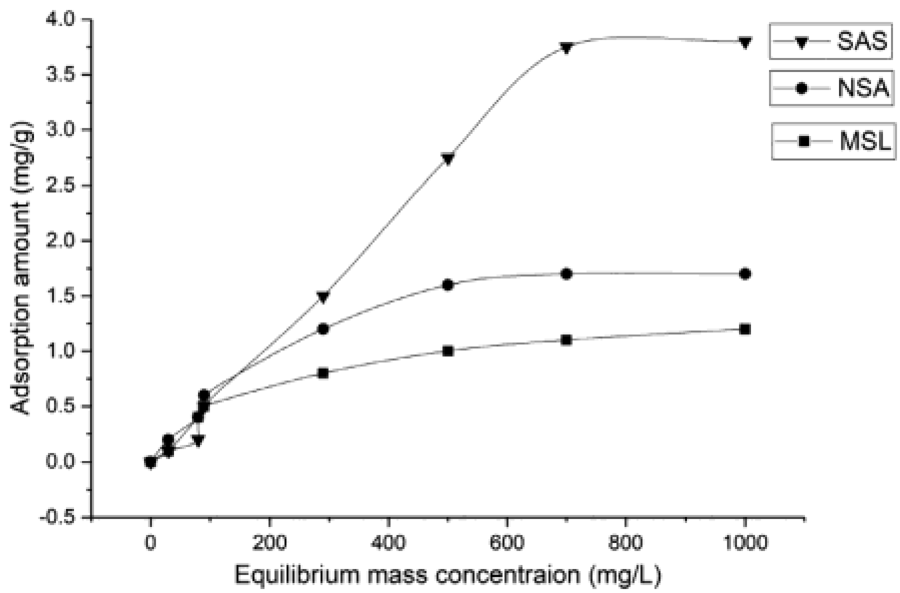


Fig. 9. Adsorption isotherms of different dispersants [44].

a good dispersant [42]. Ethanol seemed to be the most promising because heating value increased to 3613–4412 kcal/kg and the viscosity reduced to 2100–1089 cp. Different Rosin based additive prepared from dendrimer and chloractic acid through michale addition and amidation was used to stabilize CWS (Li et al. 2012) and viscosity of slurry was found to be 695mPaS. The rheological behavior of CWS depended significantly on both the nature of coal and the type of the surfactant. Slaczka et al. (2012) observed the effect of non-ionic detergents like Rokwinol 60 (polyoxyethylated sorbite oleate, $C_{64}H_{124}$ O_{26}), Rokanol LO18 (RO (CH_2CH_2O) n H, where R-alkyl radical chain containing 16–18 carbon atoms, n" is around 18, as well as anionic sodium lignosulphonate LSP (a cellulose production byproduct) on the rheology of highly loaded CWS. The prepared slurry showed pseudo plastic and dilatant properties. Besides electrostatic repulsion, the stabilization steric effect played significantly in the fluidity of CWS [43].

A comb-type molecular dispersant synthesized by copolymerizing styrene, acrylic acid and starch has been employed to investigate the physiochemical properties like Zeta potential, viscosity and static stability of CWS [44]. Rheological parameters were compared with the commercial dispersants, modified sodium lignosulfonate (MLS) and naphthalene sulfonate (NSA). When 0.5–0.6% dosage dispersant was added to CWS, there was a significant increase in the Zeta potential compared to NSA and MSL. In presence of styrene, acrylic acid, and starch, the apparent viscosity reduced to a minimum (862 mPaS). The equilibrium adsorption quantity of styrene, acrylic acid, and starch was found to be more than MSL and NSA on the coal surface due to its small contact angle with the dispersant SAS (Fig. 9.).

Two amphiphilic copolymers from 1-napthylamine-6-sulphonic acid and poly-styrene co-maleic anhydride, and by mixing both with methoxy polyethylene glycol was applied as a dispersant for CWS to investigate the rheological characteristics of CWS. It was observed that both the surfactants significantly stabilized the CWS by imparting electrostatic and steric repulsions [45]. Surface activity of dispersant candanol formaldehydes sulfonate (CFS) synthesized by sulfomethylation reaction of candanol was optimized by surface tension measurement and it significantly increased the wetability of coal in CWS [46]. It was observed that with 50% wt. of coal containing 1–1.8% CFS remarkably decreased the viscosity compared to the CWS containing lignosulfonate (SL). The static stability of CWS with 1% wt. of CFS gave a below 50% penetration ratio for up to a month.

The dispersant synthesized from sugarcane bagasse could be used to carboxymethyl cellulose (SCMC1) through acidic and alkaline hydrolysis, and characterized by FTIR and TGA. It was compared with two sodium carboxymethyl cellulose (SCM1 and SCM2) prepared from microcrystalline cellulose for its effect on rheology of CWS. They concluded that the static stability of CWS was higher with a lower apparent viscosity with SCMC1as dispersant. It may be due to the higher molecular mass and higher degree of substitution of SCMC1. Ma et al. postulated that a comb-like Polycarboxylate (PC) polymer with branched chain modified by -COOH and -$CONH_2$ groups that could impart excellent steric stabilization and inhibited coal agglomeration [48]. They synthesized the polymer by free radical polymerization of acrylic acid, acryl amide and macro-monomer. CWS prepared from bituminous coal with polycarboxylate additive exhibited an apparent viscosity of 305 mPa.s and 79.8% penetration. Thus, the dispersant had excellent effect on the fluidity and stability. A rosin-based dispersant maleopimaric acid diethanolamide (MAD), had characterized and resulted better wettability and adsorbing power compared to commercial dispersant sulfonated naphthalene formaldehyde (SNF) condensate used in CWS [49].

Stability of CWS depends upon the influence of the molecular weight of grafted sulfonated alkali lignin (GSAL) polymer [50]. A series of GSAL (modifying the molecular weight) was compared with naphthalene sulfonate formaldehyde condensate (FDN). It was found that the apparent viscosity in GSAL-3 was the least. The adsorption mechanism agreed with the Langmuir adsorption model (Fig. 10), and the adsorption quantity of GSAL decreased with increasing molecular weight, attributed to the inter-adsorption and hydrophobic effect of GSAL.

The rheology of CWS was tested with and without Triton X100 as an additive. The CWS showed shear thinning and shear thickening at lower coal loading, while above 50% coal loading shear thinning behavior stabilize CWS [47] extracted cellulose from bagasse, produced sodium only was observed [51]. Three novel dispersants namely (TIA-1, TIA-2 and TIA-3) were designed and synthesized having a 3-Dstructure with large reticulation, to stabilize CWS. Dispersants were prepared by mix- ing a commercial dispersant NDF with varying quantity of tannic acid. Electrical double layer formed by dispersant TIA-1 impacted the elec- trostatic repulsion among the coal particles and contributed to the Zeta potential value. Dispersant TIA-1 with a 3-D structure and large reticula- tion formed strong hydration film around the coal particle and provided steric as well as electrostatic repulsion in comparison to TIA-2 and TIA-3 [52]. Three low-rank coal types with varying O:C were used to prepare CWS in by adsorption of Polycarboxylate on coal surface [53]. Additionof extra polycarboxylate prevented the relative motion between the par- ticles which increased the viscosity. Thus, it was essential to judiciously

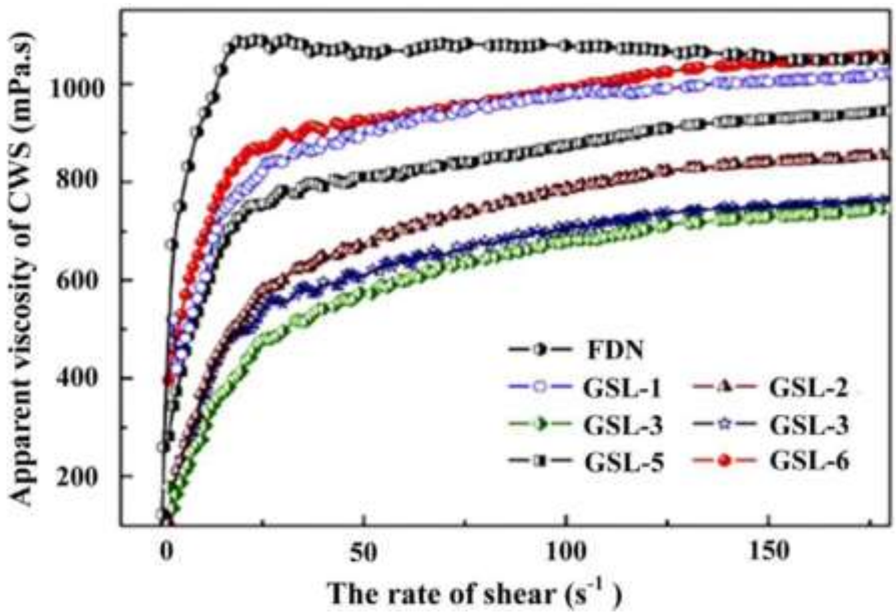


Fig. 10. Rheological Curves of CWS with 1.0 wt.% Dispersant [50].

quantify polycarboxylate dispersant in the CWS, based on adsorption. A phosphate type additive sodium tripolyphosphate (STPP) was applied as a stabilizing agent to CWS within the shear rate range of 60–160 S^{-1} , and variation of parameters like pH, solid coal loading and additive dosage. CWS behaved dilatant at lower and exhibited thinning behavior at higher solid loadings [54].

Cocking sludge and its wastewater contain many complex environmentally harmful components. To minimize such pollution the coking waste slurry and sludge of 62.16% and 61.36% concentration respectively were prepared and analyzed for application in CWS. The sludge water contained higher concentration of hydrophilic functional groups and abundant internal voids that adversely affected CWS [55]. More hydrophilic functional group in cocking waste water improves the wet ability of coal and increased the coal concentration to 0.8% in CWS [56]. They investigated the effect of adsorption of ammonia, phenol, nitrogen, etc., of coking wastewater on coal and concluded that phenol improved the wettability of coal. Wang et al. used alkaline additive for the reduction of viscosity of the CWS and stated that addition of 1% wt. of alkaline to CWS the viscosity reduced to half than without alkaline additive [57]. Change in zeta potential and microstructure of the particle were also investigated. At lower concentration of alkaline solution zeta potential reduced which means absolute zeta potential increased as well as free water in coal water slurry. Surfactants like Benzyldimethylhexadecylammonium chloride (HDBAC), Octyltrimethylammonium chloride (OTAC) and Cetyltrimethylammoniumchloride (CTAC) interacted with coal pitch and the wetting behavior, surfactant adsorb ability and Zeta potential were analyzed [58]. It was observed that with a constant surfactant concentration, the viscosity of coal pitch water slurry increased with an increase in the amount of coal pitch. Zisman theory was applied to study the wetting behavior of coal by measuring the contact angle and the surface tension, and a linear relationship found. Low-grade coal is preferred for gasification because of its abundance and lower price so proper optimization of rheological property and packing efficiency is highly essential [59]. It is observed that refined coal decreased the number of pores and polar functional group on the coal surface which was confirmed through SEM and IR analyses. Among the three dispersants, studied (NSF, PPA and SMF), PPA was the best in reducing the viscosity as well as the yield stress of CWS. It was because of its higher tendency to reduce surface tension and enhancing wettability of coal. Zhang et al. [60]. designed and synthesized a variety of polycarboxylate dispersants from various monomers and studied their perfor-

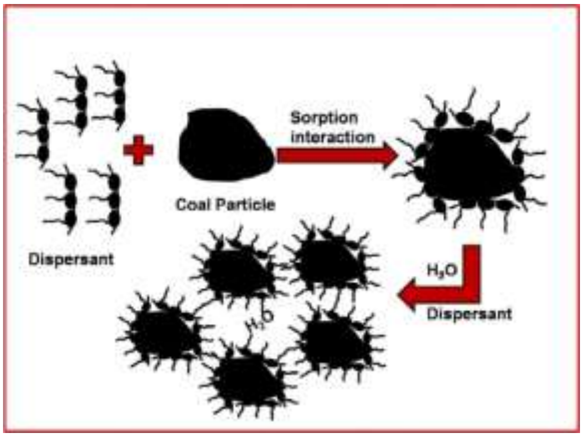


Fig. 11. Schematical presentation of adsorption mechanism of polycarboxylate dispersant in coal.

mance on a low rank China (Shenfu) coal CWS for its stability (Fig. 11).It was observed that, when the molar ratio of the monomer SSS and acrylic acid (AA) was 65:35, the dispersant performance was the best with lowest apparent viscosity (920 mPa•s) having a coal concentra- tion of 63% wt. Thus, the CWS thus prepared could satisfy the national standards well in terms of apparent viscosity, rheology and stability.

Zhang et al. compared the stabilizing ability of a novel HAP disper- sant with humic acid in preparing CWS [61]. Humic acid based poly- carboxylate was synthesized by copolymerizing HA, acrylic acid and maleic acid and was analyzed by proton NMR, thermo gravimetrically and FT-IR. The viscosity study of CWS particularly the mass ratio of HA and monomer in HAP, initiator concentration, reaction temperature and reaction time. When HAP dosage was up to 0.5% wt., the apparent vis- cosity of CWS was 505 mPa•s. and the penetration ratio reached 85.45% after 96 h, which was higher by 12.87% than that of CWS prepared with HA. Also, the CWS dewatering rate in presence of HAP was 1.85% less than that of CWS with HA.

A high-performance dispersant PC was obtained by copolymerizing HPEG, AA and AMPS and was used to prepare CWS [62]. The rheology of the CWS with the developed dispersant was compared with the NSF condensate dispersant at 0.5% wt. dosage. The developed polymeric dis-

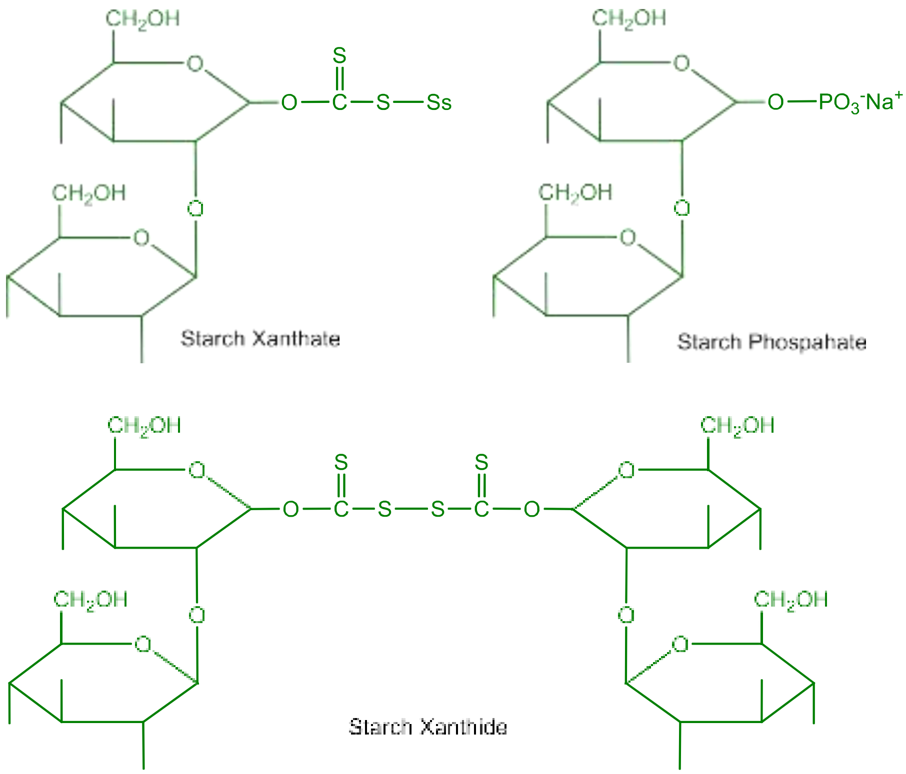


Fig. 12. Molecular structure of three starch-based additives [66].

persant provided more electrostatic repulsion force, wetting property, and steric hindrance. Effect of inorganic and organic components in wastewater can affect the stability and preparation CWS and is a utilization strategy of waste water. They postulated that, monovalent salts like NaCl, KCl etc. decreased the viscosity of CWS and bivalent salts like $CaCl_2$, $MgCl_2$ had no significant role in viscosity reduction. However, CWS containing trivalent salts like$AlCl_3$ sharply increased the viscosity, attributable to the decrease in the amount of free water with trivalent salts which adversely affected the viscosity and the rate of adsorption of the dispersant on the coal particle. Wang et al. and Mukherjee et al. studied the interfacial interactions of coal of various carbon:oxygen ratios with aqueous solution of an anionic and a non-ionic additive [63,64]. An increase in the mineral content in carbon increased additive adsorption thereby increasing the surface charge of the aqueous coal particle. Contact angle data showed that the additives modified the hydrophobicity/hydrophilicity surface chemistry of coal resulting in the release of bound water in to the bulk which decreased slurry viscosity. Thus, there was a correlation between the slurry and the free water content.

Dispersing ability of dispersant HA-g-PSSNa in which humic acid skeleton was hydrophobic and sodium styrene sulfonate side chains were hydrophilic was examined in CWS stabilization. It was observed that with an increase in length of PSSNa side chains, the dispersability of the developed polymer increased. In CWS stabilization, HA skeleton being hydrophobic adsorbedon the surface and increased the adsorption rate of HA-g-PSSNa. Thus, hydrophilic PSSNa side chains were oriented towards water to form a coating of hydration on the coal particle. It produced mechanical shock due to particle repulsion inhibiting coal aggregation [65].

Starch-based polymer additive contained large number of –OH groups (phosphate and thiol groups and disulfide linkage) which might be the main cause of viscosity reduction in CWS [66]. They formulated the performance of three starch based additives (Fig. 12) derived from starch, *i.e.*, starch phosphate, starch xanthate and starch xanthide and the rheology of CWS from three non-coking coal varieties was investigated.

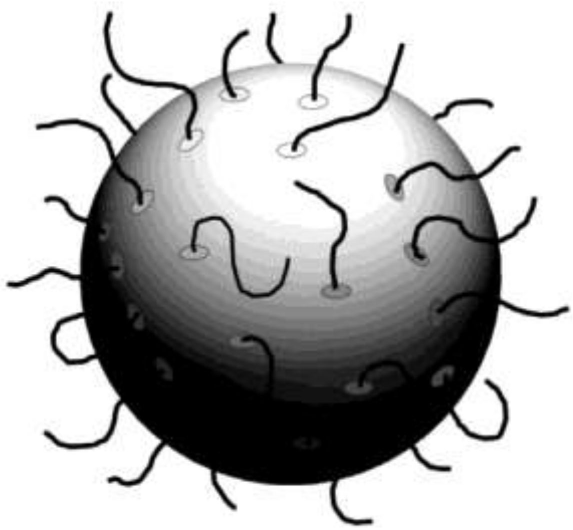


Fig. 13. Stabilization mechanism of CWS by starch xanthate additive [68].

The theological performance of these additives increased in order of starch xanthate < starch phosphate < starch xanthide [66]. When starch xanthate and starch phosphate were compared, it would develop more steric hindrance and prevent from conglomeration of coal particles more than that of starch xanthate due to the bulky nature of phosphate ion compared to xanthate ion (Fig. 13). Hence, starch phosphate proved to be a better dispersant than starch xanthate. On the other hand, if starch xanthate and starch xanthide were compared, starch units may adsorbon to coal particles simultaneously as starch xanthide contained a rigid disulphide linkage between the units. As a result, a network structure was created due to the bridging of coal particles which promoted con- glomerated the particles (Fig. 14). Being dynamic, this network structure

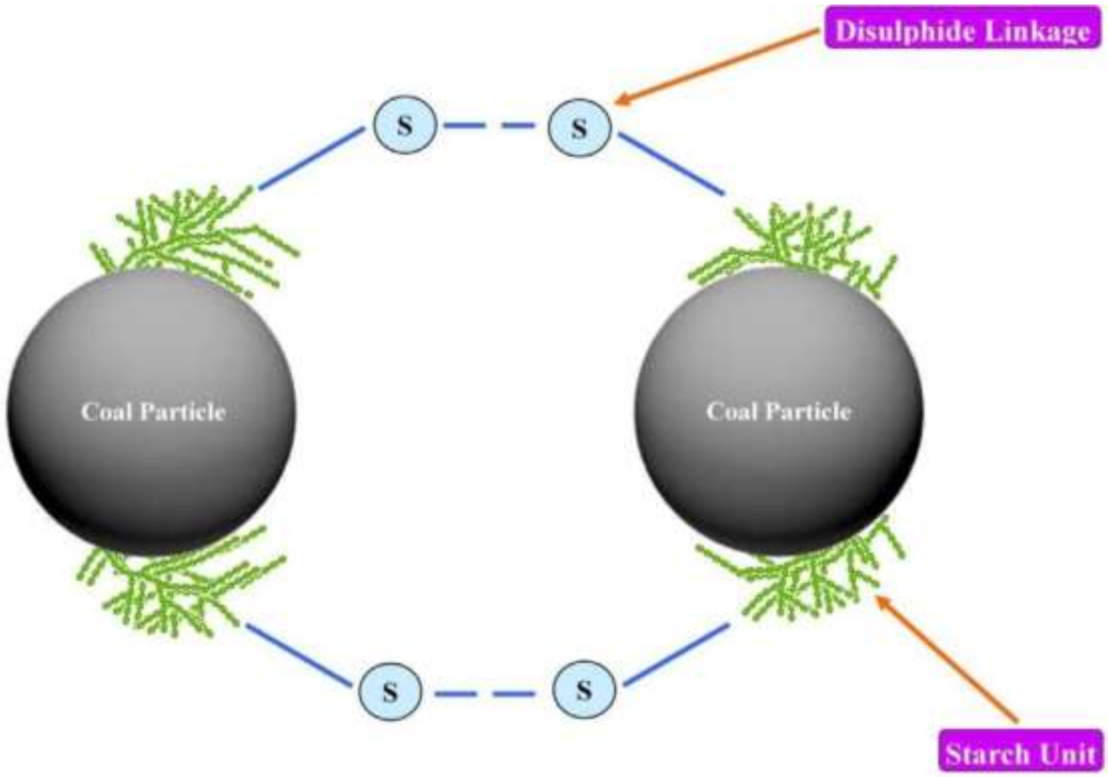


Fig. 14. Mechanism of adsorption of starch xanthide on to the coal surface [66].

was dissolved and regenerated continuously during adsorption [67]. Thus, rheological performance of CWS was less in case of starch xanthide compared to that of starch xanthate.

Starch based dispersant prepared from the radically polymerized acrylic acid and styrene sulfonate monomer exhibits excellent stabilizing tendency to CWS [69]. Static stability of CWS was observed at a coal concentration of 66% with dispersant dosages of 0.4% with the viscosity at 848 mPaS.

Natural dispersant

Saponin, isolated from the fruits of plant *Sapindus laurifolia* (a soap nut tree), has excellent surface activity and is used as natural detergent and was able to replace well known commercial dispersant in CWS stabilization. Saponin is a combination of both hydrophobic and hydrophilic unit in which glucose, xylose, galactose, and rhamnose were the sachharide combinations constituting the hydrophilic unit, and either steroids or triterpene ring constituted the hydrophobic part. The hydrophobic part is referred as glycon unit and the hydrophilic part as aglycon unit (sapogenin). Saponin isolated from *Sapindus laurifolia* was utilized as a stabilizing agent to formulate CWS up to coal concentration 64% wt. [6]. The effect of various factors like pH, temperature, volume fraction of coal, amount of dispersant, etc. was discussed on CWS rheology in the presence of 0.8% of saponin concentration. The saponin exhibited same dispersibility with that of the commercial anionic surfactant, sodium dodecyl sulfate (SDS) [70]. The stabilization mechanism may be explained by considering that hydrophobic part of saponin adsorbed on the hydrophobic coal surface where as hydrophilic part of saponin protruded towards the aqueous phase dangling in the bulk water. Such attachment is also supported from the adsorption experiment of hyderagenin (a hydrolyzed saponin product) as presented in Fig. 15.a. Thus, bulk glycosides hydration occurred and a barrier developed around the coal particle surface. This mechanical barrier provided steric repulsion and prevented from conglomeration of coal particles when they collided with each other (Fig. 15.b). The stabilization of CWS was mainly due to the steric repulsion as Zeta potential of CWS decreased with adsorption.

Similarly another saponin containing plant *Sapindus mukorossi* could be a suitable substituent of commercial dispersant in CWS formulation and stabilization [71]. Maximum stability of CWS was resulted at the critical micellar concentration of saponin. Their experimental data well fitted the Bingham plastic model. Zeta potential value of CWS decreased in the presence of saponin confirming the steric stabilization of CWS.

This saponin from extracted *A. concinna* is a triglycoside of acacia acid with both glycon and aglycon parts (Fig. 16). Stabilizing action of saponin extracted from seed and pericarp were compared. The pericarp was a better stabilizer for CWS compared to seeds [72].

The rheology of CWS followed the Bingham plastic model in pres- ence of saponin. Thus, saponin of *A. concinna* is a suitable substitute for synthetic additives (like SDS) as shown in Fig. 17. Similarly another saponin containing plant from acacia family *Acacia auriculiformis* was more effective dispersant in comparison to *A. concinna*.

Another saponin isolated from A. auriculiformis is cheap, biodegrad- able, environmentally safe, and non-hazardous and can be used as a suitable dispersant [3]. A bimodal coal sample, dispersant, A. auriculi- formis, and stabilizer carboxymethyl cellulose were used in the stabiliza- tion investigation. Out of four bimodal coal samples (Sa-1, Sa-2, Sa-3, and Sa-4), sample Sa-1 with a coarse to fine ratio of C:F::60:40 had the lowest apparent viscosity and the best stability at the optimal disper-
sant concentration (0.021 g/cm^3 and 0.010 g/cm^3 f) for aqueous and chemical extraction method respectively. In addition to the dispersant, the stabilizer concentration was set at 0.005 g/cm^3 based on the yield stress value. Because of the steric repulsions given by bulky hydrated heads, coal particle interaction is inhibited. The stabilizer connects the coal particles, forming a three-dimensional network that reduces the viscosity of the slurry and improves flowability. [3].

A combined conclusion can be drawn from [6,68,72] because of thesame component saponin is present in the plant, sapindous laurifolia [6], Acacia concinna [72] and Acacia auriculiformis [66]. Different types of

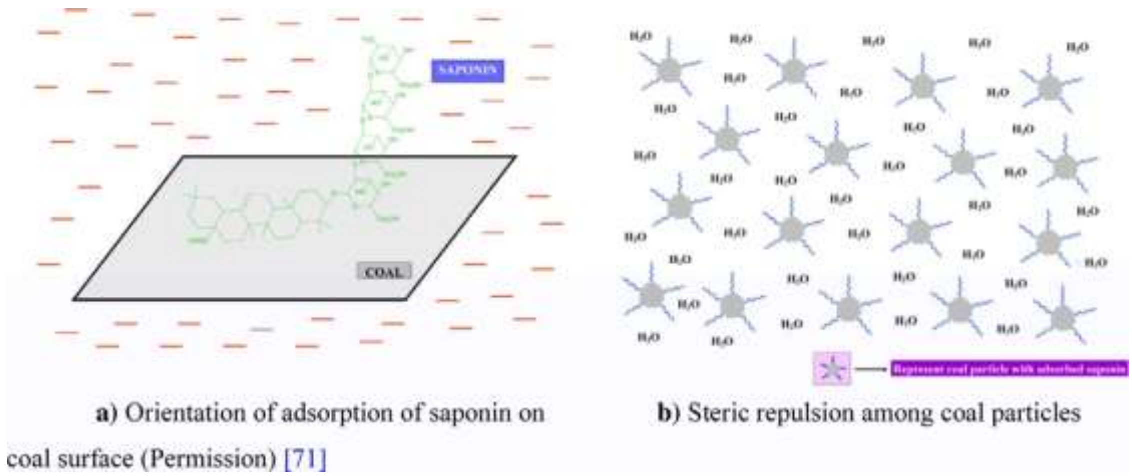


Fig. 15. **a)** Orientation of adsorption of saponin on coal surface (Permission) [71]. **b)** Steric repulsion among coal particles.

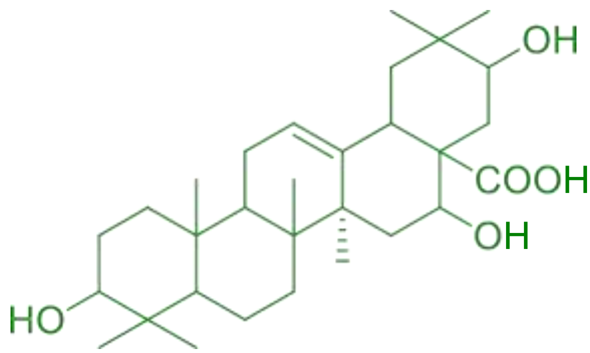


Fig. 16. Molecular structure of acacia acid [71].

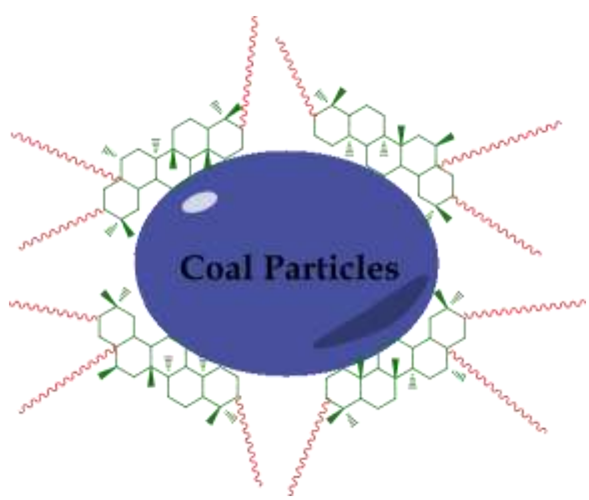


Fig. 17. Schematic representation of a coal particle with adsorbed saponin [3].

saponin are present in all the above three plant but their properties and stabilizing tendency are similar. The adsorbed additive saponin, prevent the coalescence of coal particle by modifying the surface charge of coal leading to electrostatic repulsion among coal particles; introducing bulky groups at the coal surface to introduce steric repulsion; by increasing the steric wettability of the solid surface to eliminate the hydrophobic interaction. The exposed glycon part/hydrophilic part can also be hydrated to increase the effective size of the additive for exertion of mechanical barrier.

Natural and synthetic mixed surfactant system

Surfactants mix is preferred compared to a single surfactant as it is ecofriendly, gives better result and is inexpensive [73]. The better result is due to the synergetic action of surfactants even at a lower dose. It is postulated that a nonionic surfactants mixture exhibited ideal behavior in mixing compared to anionic-cationic, ionic-nonionic due to synergism [74–76] or antagonism [77]. Das et al. formulated HCCW by mixing natural and synthetic surfactants as dispersant with low-rank Indian coal for stabilization [68]. At equimolar concentration of saponin-CTAB and 6:4 molar ratio of saponin:SDS exhibited maximum reduction in surface tension and viscosity of CWS. The hydrophobic (triterpene) part of saponin attached to coal surface through its bottom face, exposing the upper face to interact with SDS or CTAB hydrocarbon chain. Binding was more effective between the triterpenoid rings of saponin and SDS due to same number of carbon in the hydrocarbon chain compared to the CTAB-saponinbinding (Fig. 18). It is because hexadecyl of CTAB does not make a proper fit with the saponin carbon chain.

Saponin isolated from shikakai mixed with an anionic surfactant SDBS effectively stabilized the HCCWS slurry [78]. The flow characteristics of CWS were investigated at different coal loading, pH, concentration of shikakai-SDBS mix. Suitable saponin-SDBS concentration for HCCWS was determined from the surface tension and apparent viscosity value of CWS. The surface tension reduced to 14 mN/m and viscosity to 0.403 Pa.s at optimized (saponin:SDBS::92:8) concentration. Thus, shikakai-SDBS mix was superior compared to shikskai or SDBS alone. Similarly, shilakai saponin mixed with a cationic surfactant DDAB at an optimized concentration of 95:5 (saponin:DDAB) improved the flow be- havior of HCCWS significantly [79]. A synergistic interaction between the nonionic surfactant saponin isolated from shikakai with an anionic surfactant SDBS [79] and a cationic surfactant DDAB [78] decreased the apparent viscosity of CWS as well as yield stress and increased the
coal load significantly. It may be concluded that whatever may be the source or nature of saponin (either from *S. laurifolia* or from *A. concinna*) there is always a synergistic interaction between the mixed surfactant systems which resulted a decrease in apparent viscosity and increase in steric wettability and stability of CWS.

Particle size distribution

Very fine particulate slurry creates problem in the flow through pipeline. To formulate a stable HCCWS with low-viscosity coal particle, its distribution plays a very important role. Suitable particle size distribution interstices or void between coal particles can be reduced to obtain maximum coal concentration. Similarly, bigger particle size in the slurry settles down easily to deter the flow. Thus, particle size distribution is vital in preparing highly concentrated CWS. The space

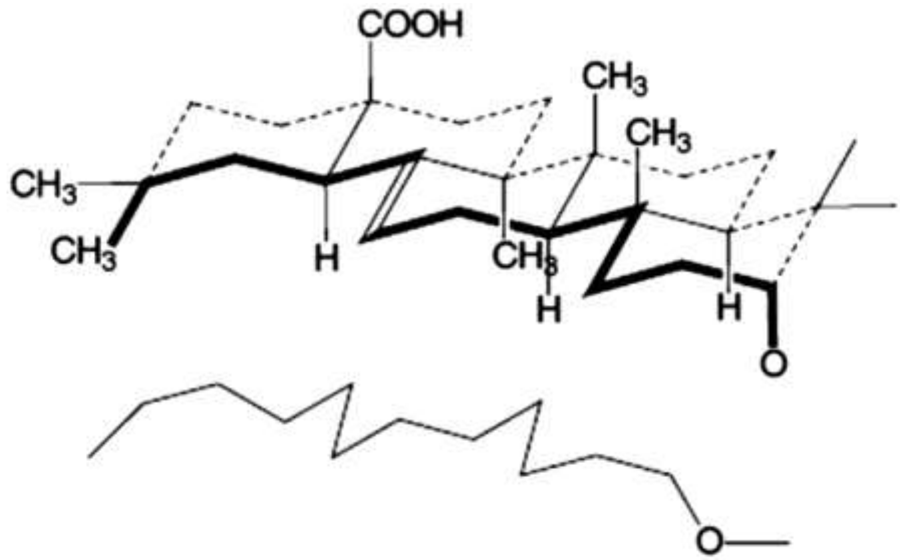


Fig. 18. Representation of aglycone part (binding site) of steroid ring of saponin [68].

between the particles is more in monomodal sample and thus the viscosity of CWS is more. In bimodal sample, the space between the bigger particles is filled up with finer particle, and so, the viscosity is less compared to monomodal sample. In multimodal sample with more than two particle size combination reduces CWS viscosity. This section discusses the works carried out by researchers on the monomodal, bimodal and multimodal samples.

Particle size distribution is an important parameter to lower viscosity of CWS [80]. Sadler and Sim introduced bimodal concept filling the spaces between the bigger particles by the fine particles to reduce the space between particles that would reduce viscosity [80]. Comparative study with 50% by weight solid concentration for both mono- and bi-modal samples showed lower viscosity in bimodal samples. Probstein et al. investigated a fine and coarse particles bimodal model of a poly-dispersed suspension with sub-micrometer to hundreds micrometers particle size Bimodal applying lubrication concept to the bidisperse suspension with a large particle size ratio. In this, the fine fraction imparted non-Newtonian characteristics whereas the coarse fraction raised the apparent viscosity [81].

The grading equation for broken solids was used to set up the bed for maximum density [82]. The space between the coarse particles could be filled up by two-grade solutions, one is intermittent grading and the other is continuous grading. Intermittent grading gave good packing than continuous grading (done with the help of commercial material). Impact of PSD and concentration on the flow properties of high ash South Australian coal was studied taking coarse coal particle size in the range of 279–325 μm and having percent concentration of 23–50. The viscosity of CWS decreased and its flow behavior modified from visco-plastic to Newtonian with an increase in the amount of coarse fraction. The viscosity was the minimum with 60:40::fine: coarse particles in bimodal CWS. Viscosity reduction in the bimodal sample was five times more than monomodal. Multimodal sample had low shear stress and high shear rate compared to fine and bimodal CWS sample. When coarse sample was added to the fine sample, the viscosity of bimodal CWS reduced [83].

Settling of particles was fast inside the pipeline in coarse sample [84]. When the fine particle percentage increased, the CWS viscosity increased creating difficulty in pumping CWS through the pipeline. Lorenzi and Bevilacqua prepared a bimodal CWS sample with low viscosity adding a surfactant for increased surface wettability [84]. Boylu et al. investigated two coals of different ranks, *i.e.*, Turkish lignite and bituminous coal from Siberia, Russia [85]. The physical and chemical properties, and the effect of Zeta potential of different (19, 25 and

50 μm) particle sizes were studied. Two mixtures, one heterogeneous and the other homogeneous were prepared. Heterogeneous mixture had more volume fraction of solid than homogeneous mixture in the CWS.It was because the void between the particles in heterogeneous mixture was filled with fine particle which increased the volume fraction.

PSD is an important determining factor for the quality of CWS. Ultrasonic method was used to detect the distribution of particles that would determine CWS quality. Ultrasonic experimental system may also be used to detect the coarse to fine particle ratio in CWS [86]. The effect of PSD and packing features of various samples ranging between 38 and 250 μm in monomodal, bimodal, and multimodal CWS. By varying the coarse and fine particles ratio, bimodal sample showed maximum coal loading (about 65% by weight) with an acceptable rheological behavior compared to the other two [87].

Different ratio coarser to fine particles fraction was mixed with wa-ter to form the slurry and the maximum packing fraction of CWS was calculated using rheological vane yield stress technique [88]. The coal loading on CWS influences the packing density of coal, a function of particle size distribution. Optimization of PSD affected the viscosity of CWS [89]. They observed the sedimentation performance of the CWS of lignite coal (< 125 μm particle size) studying the effect on the apparent viscosity at 100 S^{-1} shear rate.

The rheological behavior, the effect of PSD, and solid concentration of CWS was investigated [90]. They observed that an increase in particle size increased the CWS viscosity. At 30% concentration by weight, low- est viscosity was reached when the fine and coarse particles were mixed at various proportions. Harmadi et al. used carboxy-methyl cellulose (CMC) as stabilizer and Triton X-100 as dispersant (at 0.03–0.05% wt. concentrations for both) to study the effect of particle size distribution (#270/325–325/400) in CWS [91]. By decreasing the particle size, the slurry concentration increased by 66% wt.CWS rheology showed best fit with Herschel-Burkley model (n<1).

The rheology of CWS containing different PSD can be explained by considering four type particular interactions, *i.e.*, hard sphere, soft sphere, steric repulsion and van der waals attraction. For a stable suspen- sion, it is concluded that the maximum energy crosses the level 25KT.An effective medium theory to detect online particle size of CWS, *i.e.*, fine particle and coarse particle was established. The CWS quality could be controlled by applying three frequency methods [92]. Four different particle sizes (355–250 μm range) for varying solid concentrations (35, 40 and 45% wt.) was studied and a conclusion was drawn that maximum coal concentration of 45% wt. can be reached by choosing suitable PSD
[93] . Tu et al. used index E method to assess the packing density of bitu-

minous and lignite coal in CWS with distributed particle size by mixing the two in different proportion to obtain various packing densities [94]. Using Rosin-Rammler equation and Alfred equation for packing density, they opined that multimodal distribution of particle size is much more packing efficient than monomdal distribution. An effective medium theory model was proposed to study particle size distribution and changes by applying ultrasonic method through acoustic attenuation characterization of CWS [93]. The developed theoretical model explained the detection of CWS particle size, fine and coarse sized PSD online. Particle size distribution obtained corroborated well with other popular method.

Waterjet method in which high pressure is applied for comminution of coal to ultrafine sizes for electric power generation is a novel advanced technique. The ultrafine fractal theory was applied to quantify entire PSD of the comminuted materials to get specific and exact values [5]. They observed that the particle size distributions obtained by the high-pressure water jet showed a bifractal performance confirming the mechanisms involved in size reduction. Other approaches are surface based size reduction and volume-based size reduction. Li et al. reported an attractive method to utilize clean coal by producing ultrafine particles for CWS by coupling high-pressure water jet with cell cavitation [95]. An advantage of this was that narrow size distributed ultrafine coal particles (of <10 □m size) could be obtained, with the operating pressure and stand-off distance as the two critical factors. With an aim was to reduce the particle size and distribution to get more packed CWS with more stability Galecki prepared four categories of ultrafine particles (of −850 to <106 μm size) by comminuting the coal with water jet [96].

Effect of microwave treatment

Microwaving, a particular region of electromagnetic waves with frequency varying between 0.3 to 300 GHz of wavelengths 1 mm to 1 m, of coal is important in CWS technology to reduce energy consumption in high concentration slurry transport. Usually, thermal and non-thermal effects are two ways to utilize microwave energy. In thermal effect, microwave energy is converted into thermal energy with a complete loss of microwave energy. The mechanisms explained by considering that polar molecules of the dielectric medium during their movement in the electric field direction absorbs electric field energy and converts it to thermal energy, thus increasing the temperature of the dielectric medium. In non-thermal effect, microwave region of the electromagnetic radiation directly interact with the reactant molecules [97].

Cheng et al. investigated that polar moisture in coal absorbed microwave energy but the non-polar hydrocarbon hardly absorbed the energy when the coal sample was irradiated with 2.45 GHz energy [98]. Meilkap et al. reported that moisture could be heated approximately 100 times faster than coal [99]. Cost effective coal cleaning processes like dewatering [100] and pyrite removal [101] were performed by microwaving which increased the grinding ability [102]. In addition to reduction of inherent moisture content, microwave irradiation reformed the oxygen functional group and decreased the total surface area [103]. Thus, microwaving increased the coal concentration in CWS and improved its rheological behavior.

Microwave energy could significantly improve the flow behavior of CWS of high-ash Indian coal [104]. Ash sample was treated at high power (900 W) with exposure times of 30, 60, 90 and 120 s followed by physical and chemical analyses which altered the flow behavior and coal characteristics. Sahoo et al. developed a quadratic model and studied the effect of microwave irradiation time, PSD, coal content, and shear rate on apparent viscosity of CWS by applying central composite design (CCD) theory [104].

Sahoo et al. studied the combined effect of microwaving and artificial network approaches on the rheology of CWS and postulated that microwaving lowered the apparent viscosity of coal with a pseudo-plastic behavior [105]. Further, there was an exponential decrease in apparent viscosity and an increase in shear rate. They used back-propagation ANN model to establish a relationship between the rheology and apparent viscosity. The correlation coefficient (R^2) values of 0.99 confirmed that ANN model could exactly predict the apparent viscosity of CWS.

Zhou et al. prepared a HCCWS by upgrading Shengli lignite from In- ner Mongolia, China for combustion and gasification through microwav- ing. They used various technique like-IR, contact angle measurement- ray diffraction spectroscopy, N_2 adsorption porosimetry, scanning elec- tron microscopy to investigate the surface morphology and functional groups in the upgraded lignite. They observed that microwaving in- creased coalification and decreased hydrophilicity as a result of which the maximum coal concentration increased from 45.6 to 51.7% wt. It may be due to the removal of free moisture and increase in the contactangle or hydrophobicity [106].

Song et al. did thermo-gravimetric analysis of three-stage mi- crowaved high moisture lignite of Inner Mongolia. In the first stage the surface temperature increased which reduced slightly in the sec- ond stage and rose again in the third stage. The fine lignite coal par- ticle having <0.2 mm diameter and lump particles of 10 mm size dried efficiently than the granular lignite of 1–2 mm size range [107]. Mi- crowaving performed on lignite blended separately with a thin layer of 10% sodium sulfate, sodium carbonate and coal fly ash exhibited dielec- tric loss in dried lignite, raw lignite, lignite-coal fly ash, lignite-Na_2SO_4 and lignite-Na_2CO_3 at 2450 MHz were 0.06, 0.13, 0.14, 0.15, and 0.18 [108]. Increasing temperature of the thin layer coat on lignite could af- fect moisture removal rate. The average temperature of the thin layer coated lignite at 385 W was about 10, 7, and 2 °C when blended with sodium carbonate, sodium sulfate, and fly ash. Thus, sodium carbon-
ate is preferred followed by sodium sulfate and fly ash among the three additives.

Ren et al. studied the interfacial properties of lignite CWS on the solid concentration and static stability by varying microwave duration. By increasing the irradiation to 12 min, the surface hydrated film on lignite became thinner and solid concentration increased from 51.63 to55.30%. It resulted in decreased moisture and oxygen-containing func- tional groups thereby forming a smooth surface. As a result, the pseudo- plasticity improved, yield stress of LWS reduced and more amount of dispersant could be adsorbed [109].

Up gradation efficiency in terms of slurry ability and solid con- centration increases in lignite by adding lignite semi-coke which is a microwave absorber. Increased microwaving duration removed mois- ture, carboxyl and hydroxyl functional groups and porosity [110]. These decreased the apparent viscosity of LWS to 1000 mPa. and increased the lignite concentration from 49.49 to 63.90% wt. Besides reducing the inherent moisture content, microwaving significantly increased the calorific value and fixed carbon content. Such upgrading strategy also generated microspores in the coal while increasing the pore volume and surface area. Similar result was reflected in terms of decrease in the value of oxygen:carbon ratio [111].

Ultrasonic radiation

Ultrasonic wave consists of compression and rarefaction and the cy-cle that leads to the generation of cavitations of bubbles. Applying ultra-sonic wave is useful in carrying out chemical reaction in both homoge-neous and heterogeneous systems. Ultrasound radiation produces high transient temperature and pressure due to localized collapse of acousticcavitations [112]. Depending on ultrasound features, it is applied in var-ious coal cleaning processes such as desulfurization, liquefaction[113]and coal extraction [114]. Cavitations bubbles due to ultrasonic wavecollapsed in specific environment with extremely high temperature and pressure, producing high velocity interparticle collision [115] thereby enhancing the dispersion of solid particle in liquid-solid solution system.

Guo et al. analyzed the adsorption of additive developed from naph- thalene oil before and after ultrasonication. The saturated adsorption of additives was more with irradiation compared to its absence. The ad- sorption of different additives in coal agreed with Langmuir adsorption model irrespective of the ultrasonication which indicating an adsorption monolayer [115].

$$q_e = q_m K C_e / (1 + K C_e)$$

where, q_e = Saturated amount of adsorption (mg/g)

K = Adsorption parameter

C_e = Equilibrium concentration (mg/L) q_m = Maximum adsorption amount (mg/g)

Zeta potential value shifts towards more negative after 5 min radiation at the ultrasonic intensity of 60 w/cm^2 [115]. Static stability is also improved by ultrasonic radiation. Wang et al. applied ultrasonic radiation on two types of slurries of petroleum coke and paraffin oil. Results indicated that application of ultrasonic radiation significantly decreased the apparent viscosity of both slurries and markedly improved their static stability. With increase in petroleum coke concentration, there was a decrease in apparent viscosity and static stability was resulted. They concluded based on observed optimum ultrasonic treatment time *i.e.*4 min to decrease apparent viscosity and improving static stability [116].

The rheological behavior of CWS changed from dilatants flow to pseudo-plastic at a frequency of 20KHz by increasing the intensity and time of ultra-sonication [117]. It is postulated that Ultrasonic radiation resulted in a slight increase in the apparent viscosity of CWS with Improved rheology, static stability which are related to the change in coal particle size distribution dissolved in CWS [118]. Ultrasonic radiation caused an increase in specific surface area of coal which was the principal factor for the change of saturated absorption of additive on coal particle. The anionic additive was more favorable than non-ionic counterpart in improving the stability of CWS under same condition. Li and Li studied the absorption characteristic of additive on coal surface by ultrasound radiation [117]. Ultrasonic radiation could increase the dissolved ion in CWS [118]. Effect of several electrolytes like NaCl, $CaCl_2$, and $FeCl_3$ on combination ultrasonic radiation was investigated for the role of dissolved ions on the rheology of CWS. Xue et al. determined slurry concentration in CWS by combining theoretical analysis and experimental study using modified Urick equation and velocity of ultrasonic wave. They applied 3–12 MHz frequency range to calculate PSD at varying volume fractions. This method brings the possibility of using ultrasound to measure slurry density online [119].

Suspension temperature

Fluid viscosity depends on the rate of movement of solid particles in the dispersion medium. The kinetic energy of particles increases when the system temperature increases, and so the particles inside the system have more potential to move. So, the intra-particle cohesive force decreases as slurry temperature increases, and the dissolving capacity of dispersant increases. A decrease in the yield stress of CWS raises the temperature, an essential condition for economic pipeline transport of CWS [120]. Das et al. [66] studied the effect of temperature variation on the apparent viscosity of CWS taking saponin as a dispersant isolated from *Sapindus laurifolia*. The main cause of reduction in viscosity of CWS could be attributed to an increase in the kinetic energy of coal particle and fast movement of the attached hydrophilic sugar unit chain of saponin [121]. Following two equations represent the relationship between viscosity and temperature:

$$\eta = A \exp(E/RT) \quad (1)$$

$$\ln(\eta) = E/RT + \ln(A) \quad (2)$$

where, A = fitting parameter, R = Universal gas constant, η = apparent viscosity at a particular shear rate, T = temperature in Kelvin, and E = activation energy.

Temperature change also affected the apparent viscosity of fly ash in presence of natural surfactant shikakai [121] and *Sapindus laurifo- lia* [122]. According to Patanaik et al. a decrease in the cohesive force

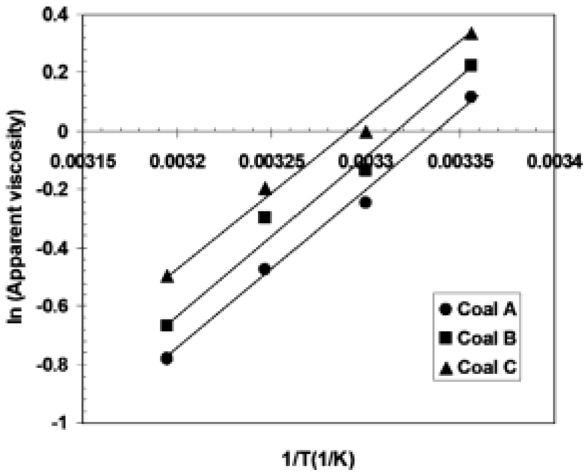


Fig. 19. Plot of logarithm of apparent viscosity *vs* reciprocal of temperature [6].

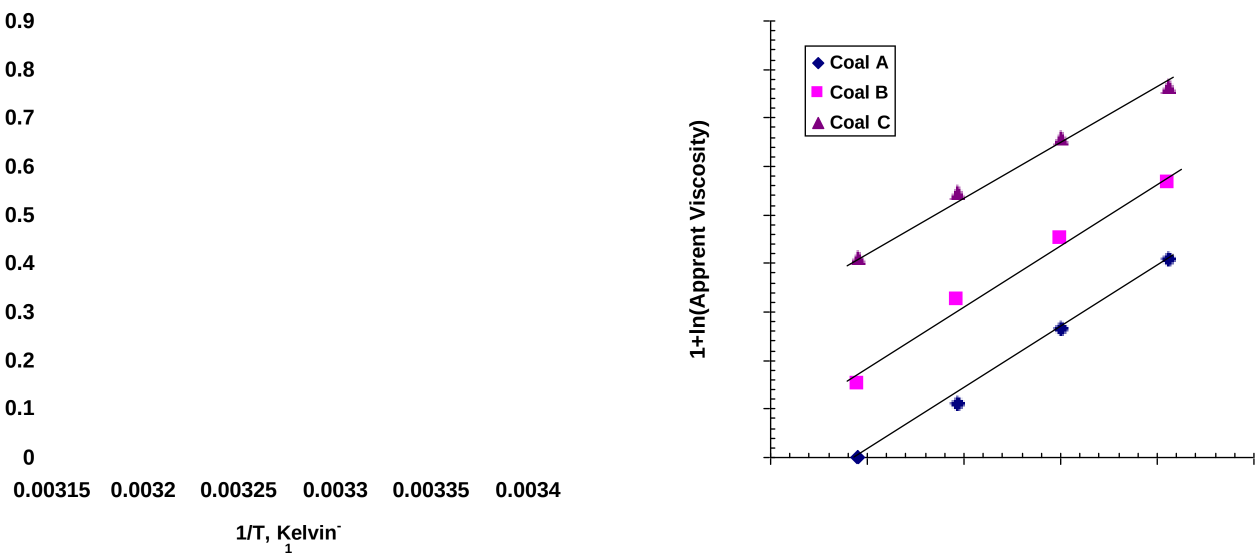


Fig. 20. Plot of logarithm of apparent viscosity *vs* reciprocal of temperature [66].

among the ash particle reduced the apparent viscosity of CWS [121]. Effect of temperature on the flow behavior of fly ash slurry was investigated below the CMC of surfactant, and reported that the effect of temperature is less significant when the surfactant concentration is below the CMC [122]. The natural-synthetic mixed surfactant system exhibits similar type of variation of apparent viscosity with temperature [68].

It is reported that after a certain minimum temperature, the flow behavior index becomes too small and CWS exhibits stronger on - Newtonian tendency. The minimum temperature depends on the nature of coal, packing fraction of CWS, and the type and amount of dispersantor stabilizer additive [123].Fig. 19

Guzman-Andrade equation describes the dependence of temperature on apparent viscosity and is widely applied in liquid-liquid and solid-liquid solution systems (Eqn (3)). It has an important application in CWS. The plots are shown in Fig. 20.

$$\eta = A_1 e^{A_2/T} \quad (3)$$

where, T = absolute temperature of slurry and A_1, A_2 = generated con- stants that give the following equation:

$$\ln\eta = \ln A + (A_2/T) \quad (4)$$

Mosa et al. 2008 [38] investigated the variation in the shear stress and rate at varying temperature, and postulated that CWS exhibited

( )

nearly a Newtonian fluid behavior at higher (180°F; 82.2 °C) temperature.

3. Discussion

Water-energy nexus in coal and coal water slurry processing

In present global scenario, the demands of energy and water resources have increased in consequences of rising urbanization and economic growth and there exists a close interrelation between, the either of the sources (energy and water systems). Water is used as the major sources for generating power and as the key supplement in various processes including extraction, refining, making slurry and its pipeline transportation, generation of electricity and biomass feedstock growth. The water-energy nexus defines the relationship between the amount of water used to generate and transfer electricity and the amount of energy necessary to collect, purify, move, store, and dispose of water in coal and coal water slurry plants [124].

Both water and energy consumption can be well regulated for a specific output and productivity by considering the critic factors such as cost optimization over the adopted technology, availability of water and energy resource and shipping. However in-depth and concentrated effort is to be devoted for providing suitable scientific recommendations for reducing the negative environmental outcomes of the widespread usage of coal by-products. Despite its benefits, the widespread use of coal by-products has unavoidable negative environmental consequences. The development of innovative technologies for large-scale and high-value-added by-product usage, with the goal of forming the industrial chain and building a circular economy, is critical [125]. As of now, there are many works have been undertaken by the researchers on the use of water source as the suitable supplement on making slurry of coal as well as fly ash for the beneficiation prospective. The slurry stabilization and its pipeline transport becomes an emerging area of work that not only for beneficiating the low grade minerals but also utilization and management of waste(s) in an economical way.

Jeffrey J. Urban et al. [126] investigated the scientific backdrop of the water-energy nexus and proposed about the adoption of emerging technologies affecting on the future of extracting energy from water. Researchers are engaged on developing processes by incorporating an improved strategy to enable a sustainable water and energy future, teetering on the steep slopes of demand curves for water and energy inevitably. However, for sustainability to be realized, these new technologies must be combined together keeping in view of the use of public attitude of water consumption and reuse.

Evaluation and optimization of the flocculation-sedimentation-filtration process for addressing water-energy nexus concerns at the Kemper IGCC power plant was investigated by Bhagavatula et al. [127]. The incorporation of a flocculation-sedimentation process prior to filtering was studied on a bench and pilot scale to improve the recycled process water quality. A polyamine-based polymer (PT318) with a dosage of 54 ppm was found to be the most effective at removing more than 97 percent of the fine coal particles through sedimentation. Pilot tests were conducted using data from bench scale experiments in order to deploy the procedure in a commercial recovered water system.

4. Overview and futuristic application

As far as fossil fuel is concerned, Coal is the largest fossil fuel resource which currently meets about 60% commercial energy requirement in the country like India. Advanced coal utilization technologies have been developed to address about the energy and environmental demand of 2st century, which utilizes the coal resources more efficiently and economically. At present CWS acts as one of the best promising alternative fuel for power generation in India. CWS fuel technology appears as an immediate attention as compared with pulverized coal. Moreover, the development of the above technology can conveniently be handled in a similar to the way and steps are being adopted on studying the stabilization behavior of the heavy fuel oil. The highly concentrated coal-water slurry (HCCWS) behaves like liquid fuel during combustion and it is economically more viable than pulverized coal. On the other hand, the additional advantage is of preventing on the storing issues without any danger of coal dust explosion and so as health hazard concern with substantial transportation through pipeline. Accordingly, this technology has been successfully adopted at the commercial scale of operation for transportation and combustion of coal, especially at the sector of power generation. The noble aspect of the CWS technology is of the usages ofthe additives which mainly includes either of commercial one and/or natural kind. Keeping in view of the green technology and eco-friendly approach the major processes is being developed in this domain is devoted on using natural additives on various slurry stabilization study. The other issue of avoiding the commercial and/or synthetic additivesis of their adverse environmental effect. It is being experienced that the use of synthetic additives is highly hazardous in nature and the more content of the sulfur found chemical additives causes harmful effect to the environments, as they substantially liberated as SO_X during com- bustion process leading to create environmental pollution. In contrast, the natural additives are comparatively inexpensive in compared to the commercially available surfactants and have almost minimized level of environmental concern upon their usages. In concern with the econ- omy of the additives, the natural additive which is to be recovered from seed/fruit which is of nominal cost is readily available at the local places as usually these additive based fruits are found in the forests and there- fore to obtain only the charges incurred about its collection. In fact, the estimated cost of a fruit of such additives is ~3 US dollar per 100 kg additives which is being adopted for slurry stabilization at the country like India. The saponin which is the key component usually obtained af- ter extraction through chemical means may cost around $15. The same scale if compared with commercial sources, it may require around $50 to obtain the additives for CWS investigations. The mixtures of natural surfactant-commercially available surfactants are sometime potentially applied in the CWS processes and in consequences it showed promising over the individual surfactants due to the formation of a rigid adsorbed layer at coal-water interface and less exposure of the coal surface to bulk water in presence of surfactant mixture compared to the individual sur- factants. It was noticed that the resulted viscosity of the slurry in pres- ence of mixtures are also lesser than that in presence of the individual surfactants. Therefore, a suitable combination of either of additive doses with the incorporation of preferential adoption of natural surfactant is highly warranted in order to develop an economical as well as environmentally friendly CWS technology for smoothening of the pipeline transport.

5. Conclusion

Pipeline transportation of coal to the power plant in an aqueous form is an ideal strategy with critical features of process economy and eco- friendly prospective. To ensure the effectiveness of coal as a fuel, the stability of the concentrated slurry should be considerably larger withan acceptable range of the slurry viscosity <1000 mPa. As the coal con- glomeration at high concentration hinders pipeline transportation, ac- cordingly incorporation of a suitable dispersant having high stabilizing feature with a lowering of slurry viscosity in the CWS processes is urged. These adopted additives are of chemical or biological origin, and some- time the combination seen to play an important role on CWS stabiliza- tion process as evident from the proposed processes. The origin of the adopted surfactants, their nature, associated interaction mechanism of additives with CWS particles are extensively reviewed and reported. In addition, the factors such as surfactant concentrations, particle size and temperature noticeably seen to be affecting on CWS stabilization process and so as the smooth transportation of the CWS, were comprehensively discussed and summarized. Some of the key outcomes exclusively based on the above reported processes and successful practiced methodology in CWS stabilization and pipeline transportation are summarized below;

1 Synthetic additives are hazardous, especially sulfur-containing chemical additions are particularly damaging to the environment, as they increase SO_X emissions during combustion and cause pollution. Use of natural or biological origin additive (surfactant) is found to be more environmentally friendly due to its chemical nature as contains only hydrocarbons.
2 The use of synergistic mixed surfactant system becomes more causative on coal loading as well as stability of the CW Slurry. Due to the formation of a rigid adsorbed layer at the coal-water interface and less exposure of the coal surface to bulk water in the presence of surfactant mixtures compared to individual surfactants, mixtures of natural and commercially available surfactants are found to be more effective than individual surfactants. The viscosity reduction of the studied slurry system is reportedly more pronounced with supplement of mixed surfactants over individual surfactant(s).
3 The role of PSD in CWS appears to be critical and have high impact at the stabilization behavior of the slurry. Mono, bi- and multi-modal PSD of coal was used in the preparation of CWS in which bi- and multi- modal PSD gives better result because of increase in the coal concentration as well as the stability.
4 Advanced techniques like ultra-sonication and microwave treatment showed to be highly effective at the modification of the coal surface for a cleaner coal with suitable rheological characteristics. One of the important applications of these methods could possibly effectively reduces the sulfur and moisture content from the coal surface and leading to increase the utilization of CWS in a cleaner way.
5 The enhancement of temperature in the CWS system appears to be more promising unlike other process parameters by reduction of viscosity of CWS to attain the acceptable level of slurry.

Overall, the HCCWS is appears to be an alternate combustible fuel and it's of more economical and eco-friendly than the pulverized coal. The convenient transportation of CWS from the mine itself thorough pipeline, and its easy storage in the power plant before use makes this process supper viable as compared the conventional one. Apart of the easy transport through pipeline, the other key benefit of CWS includes coal dust explosion minimization and minimization of the environmental pollution caused thereof and that could not only curb the health hazards but also significantly reduces the life risk among workers engaged on coal processing activities. The practiced approaches on Coal process comprises the adoption of green reagents on CWS stabilization study, development of the process intending to the minimization of air pollution and benefaction of coal resources through various proposed pipeline transportation route in an environmental friendly and economical way assures to be one of the promising advanced technology on driving of clean energy out of the one of the most demanding sources like Coal in the recent word.

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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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