INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF ÇAYIRHAN COAL-WATER MIXTURES

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ABSTRACT

INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF ÇAYIRHAN COAL-WATER MIXTURES

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In this thesis, coal-water mixtures (CWM) with Çayırhan lignite were prepared to optimize the parameters of CWM having an ideal behavior which means that at maximum coal loading, relatively stable at static and dynamic conditions and exhibit low viscosity. For this purpose, the effect of the parameters such as pulp density, amount of chemical agents, particle size distribution, addition of methanol and pulp pH were investigated. Results showed that increasing pulp density negatively affects viscosity and allowable maximum pulp density was obtained as 60% when the particle size distribution has a d_{50} value of 22.82 µm. The optimum amount of chemical agent was found as 0.9%, having 10% Na-CMC (Sodium Carboxymethyl Cellulose) and 90% PSS (Polystyrene Sulfonate). Minimum viscosity was achieved when the pulp pH was in natural conditions (pH=6.85). Addition of methyl alcohol increased the viscosity of CWM.

Keywords: Coal-water mixture, rheology, viscosity

ÖZ

ÇAYIRHAN KÖMÜR-SU KARIŞIMLARININ REOLOJİK ÖZELLİKLERİNİN İNCELENMESİ

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Bu araştırmada, Çayırhan linyitleri ile hazırlanan kömür-su karışımlarının(KSK) ideal davranış göstermesi için gerekli parametreler optimize edilmeye çalışıldı. KSK için ideal davranış, maksimum kömür yüklemesinde statik ve dinamik koşullarda kararlı ve düşük viskozite özellik göstermesidir. Bu amaçla, pülp yoğunluğu, kimyasal maddelerin miktarı, tane boyu dağılımı, metanol eklenmesi ve pülp pH ı parametrelerinin etkisi incelenmiştir. Sonuçlar vizkozitenin pülp yoğunluğunu olumsuz etkilendiği gösterdi ve d_{50} değeri 22.82 μm olan tane boyu dağılımında en yüksek pülp yoğunluğu olarak %60 elde edildi. Optimum kimyasal madde miktarı %0.9 (%10 Na-CMC ve %90 PSS) olarak bulundu. En düşük viskozite pülp pH'ının doğal değerinde elde edildi (pH=6.85). Metil alkol eklenilmesinin viskoziteyi artırdığı gözlendi.

Anahtar Kelimeler: Kömür-su karışımı, reoloji, viskozite

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THE TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

CWM	Coal- Water Mixture
Na-CMC	Sodium carboxymethyl cellulose
PSS	Polystyrene sulfonate
HCl	Hydrochloric acid
NaOH	Sodium hydroxide
γ	Shear rate (s^{-1})
τ	Shear stress (dyne cm^{-2} or centipoises s^{-1})
η	Viscosity (centipoises)
dv/dx	The velocity gradient (sec^{-1}).
F/A	The force per unit area (N/m^2 or $dynes/cm^2$).
O/C	Oxygen/Carbon ratio
O_{OH}	Hydroxyl Oxygen
O_{COOH}	Carboxyl Oxygen
SRC	Shear rate constant (0.34 for the used instrument)
n	Rotational speed (rpm)
VTC	Viscosity torque constant (1.0 for the used instrument)
SMC	Spindle multiplier constant (25 for the used instrument)
T	Torque (dyne cm^{-2})
d_{50}	50% passing particle size, µm
µm	micron
ml	mililiter
g	gram
MWe	Megawatt electrical

CHAPTER 1

INTRODUCTION

The rapidly increasing energy consumption in today's world makes it a necessity to get the best out of our lignite. With the increasing of mine mechanization and/or coal washing processes, coal finer increases rapidly and they cause some environmental problems. That's why we have to consider using lignite fines which is an outcome of various processes.

There are three ways to use coal fines. These are;

- * combustion of pulverized coal
- * briquette
- * coal-water mixtures.

The first oil crisis in 1973 turned all interests on coal converge technologies. The aim was to replace the fossil carbon in mineral oil by the carbon in coal. From this time, extensive studies have been started particularly on coal gasification, liquefaction and combustion. In addition to these existing extensive studies, in recent years, research on coal-water mixtures (CWMs) was commenced (Aktaş and Woodburn, 2000).

A typical coal-water mixture consists of;

- * 50-75% finely ground coal, with a top size of 250 to 300 microns.
- * 25-50% water
- * approximately 1% chemical additives

Ideal CWM with maximum coal loading should be relatively stable at static state and dynamic state with a low viscosity. Rheological behaviour will also affect the atomization of CWM to combustion chamber of power plant.

Viscosity is one of the most important rheological properties, and it is required to be as low as possible with the highest allowable pulp density for pumping and atomization to the boiler for a better combustion. It also affects the economics of the process because the lower the viscosity, the higher the amount of solid particles that can be loaded to the slurry (Hiçyılmaz et al., 2006).

CWM is a new kind of fuel suitable for large and industrial power plants. The practical interest in this kind of fuel is due to its technological and economical aspects. Fuel deposits are usually far away from the consumption sites. A CWM has several advantages in comparison with regular micronized coal fuel. These fluidized reactive mixtures can be transported over long distances through pipelines, safety requirements are met, and burning of this fuel yields less contaminants oxides of sulfur, nitrogen etc. Special storage and transportation are not required so loading and unloading costs are considerably reduced. Therefore, expensive heavy oil may be substituted by CWM fuel (Burdukov et al., 2002).

Lignite is the primary energy source of Turkey. High amount of lignite fines are produced during mining and washing processes and these fine lignite particles can not be easily handled, stored and transported. These particles also cause environmental problems, such as air and water pollutions. Using lignite fines as CWM has many advantages such as transportation, saving in environmental pollution, storage, but in Turkey, there is not any plant that uses CWM as fuel although in many countries such as USA, China, Italy, Sweden, Canada, Japan and Russia, CWM preparation processes were developed and used commercially in large-scale plants.

The object of this thesis was to investigate the possibility of Çayırhan CWMs with high pulp density and low viscosity. In this respect, the parameters such as pulp density, amount of chemical agents, pulp pH, particle size distribution of the feed and addition of methyl alcohol on the viscosity of CWMs, were studied.

CHAPTER 2

GENERAL INFORMATION ABOUT RHEOLOGY

Rheology is defined by Webster's Dictionary as "The study of the change in form and the flow of matter, embracing elasticity, and plasticity". It has been suggested that rheology is the most sensitive method for material characterization because flow behaviour is responsive to properties such as molecular weight and molecular weight distribution.

Rheological measurements allow the study of chemical, mechanical, and the thermal treatments, the effects of additives. They are also a way to predict and control a host of product properties, end use performance and material behaviour.

A high viscosity liquid requires more power to pump than a low viscosity one. Knowing its rheological behaviour, therefore, is useful when designing pumping and piping systems (Brookfield Catalog).

Viscosity is defined by Brookfield Catalog as "The measure of the internal friction of a fluid, caused by molecular attraction, which makes it resist a tendency to flow." This friction becomes apparent when a layer of fluid is made to move in relation to another layer. The greater the friction, the greater the amount of force required to cause this movement, which is called "shear". Shearing occurs whenever the fluid is physically moved or distributed. Highly viscous fluids, therefore, require more force to move than less viscous materials (Brookfield Catalog).

$F/A = \eta \, dv/dx$

η is a constant for a given material and is called "*viscosity*".(poise)

The velocity gradient, dv/dx, is a measure of the change in speed at which the intermediate layers move with respect to each other. dv/dx describes the shearing the liquid experiences and is called "*shear rate",* and symbolized as "γ" (sec^{-1}).
The term F/A indicates the force per unit area required to produce the shearing action. It is referred to as "shear stress", and symbolized as "τ", (N/m^2 or $dynes/cm^2$).

The final formula; $\eta = \tau / \gamma$

The fundamental unit of viscosity measurement is “poise”. A material requiring a shear stress of one dyne per square centimeter to produce a shear rate of one reciprocal second has a viscosity of one poise, or 100 centipoise.

Fluids have different rheological characteristics that can be described by Viscometer measurements. There are two categories of fluids; Newtonian and non-Newtonian fluids. Types of fluids were shown in Figure 1.

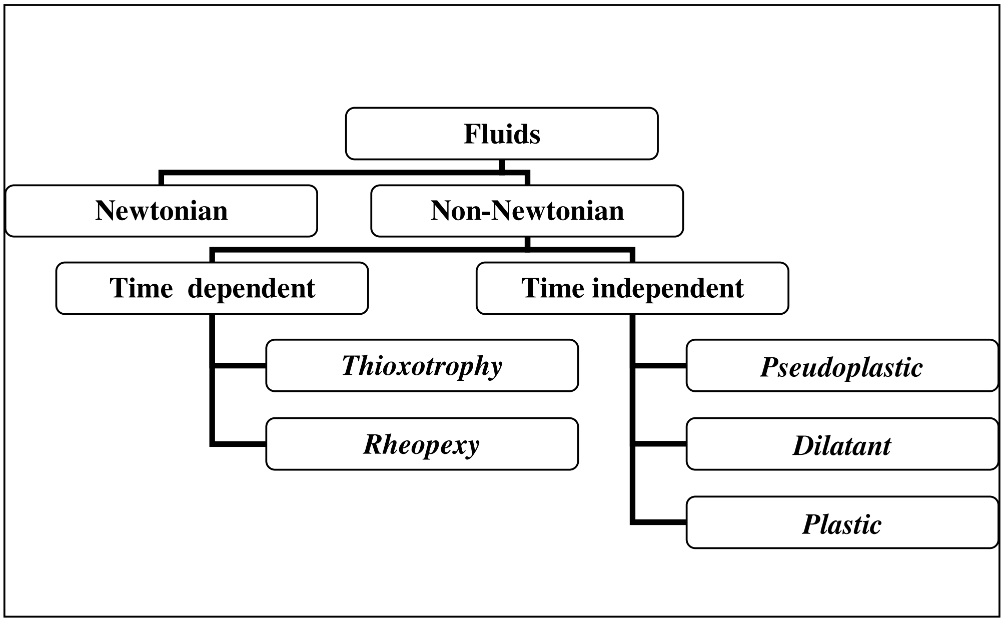

Figure 1. Types of fluids

2.1 Newtonian Fluids

Newton assumed that all materials have, at a given temperature, a viscosity that is independent of the shear rate. This type of flow behaviour which Newton assumed for all fluids is called, *Newtonian*.

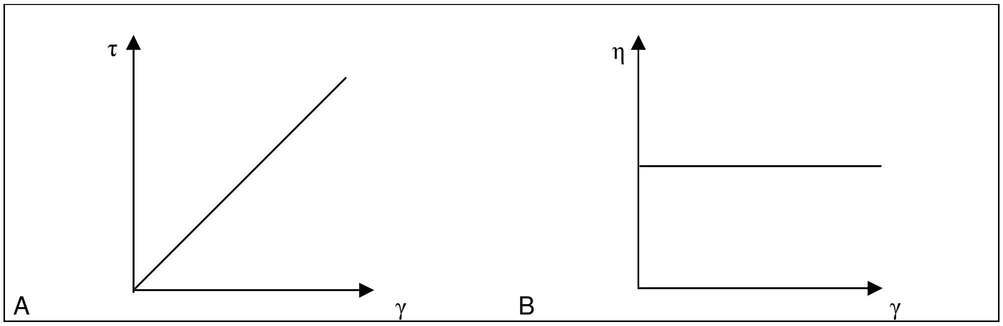

Figure 2. Flow curves for Newtonian fluids

A Newtonian fluid is represented graphically in Figure 2. Graph A shows that the relationship between shear stress (τ) and shear rate (γ) is a straight line. Graph B shows that the fluid's viscosity remains constant as the shear rate is varied. Typical Newtonian fluids include water and thin motor oils.

2.2 Non-Newtonian Fluids

A non-Newtonian fluid is defined as one for which the relationship τ / γ is not a constant. When the shear rate is varied, the shear stress doesn't vary in the same proportion. The viscosity of fluids will change as the shear rate is varied. Thus, the experimental parameters of Viscometer model, spindle and speed all have an effect on the measured viscosity of a non-Newtonian fluid. This measured viscosity is called the “apparent viscosity” of fluid.

Non-Newtonian flow can be envisioned by thinking of any fluid as a mixture of molecules with different shapes and sizes. As they pass by each other, as happens during flow, their size, shape, and cohesiveness will determine how much force is required to move them. At each specific rate of shear, the alignment may be different and more or less force may be required to maintain motion.

There are several types of non-Newtonian flow behaviour, characterized by the way a fluid's viscosity changes in response to variations in shear rate.

2.2.1 Time Dependent non-Newtonian Fluids

The time dependency is the time that held at a given shear rate (rpm). These are non-Newtonian, and when the viscometer spindle speed changed, a different viscosity is obtained. These fluids display a change in viscosity with time under conditions of constant shear rate.

2.2.1.1 Thixotropy

A thixotrophic fluid undergoes a decrease in viscosity with time, while it is subjected to a constant shear rate. Figure 3 shows the flow behaviour of thioxotrophic fluids.

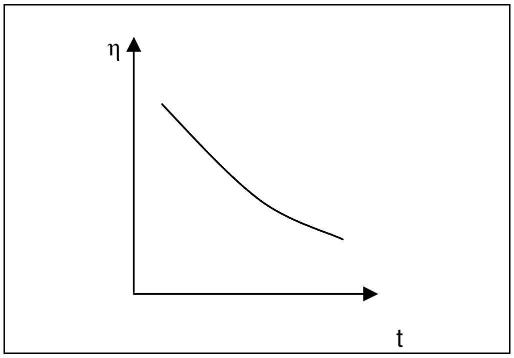

Figure 3. Flow curve for thixotrophy

2.2.1.2 Rheopexy

This is essentially the opposite of thixotrophic behaviour, in that the fluid's viscosity increases with time as it’s sheared at a constant rate. Figure 4 shows the rheopexy flow behaviour.

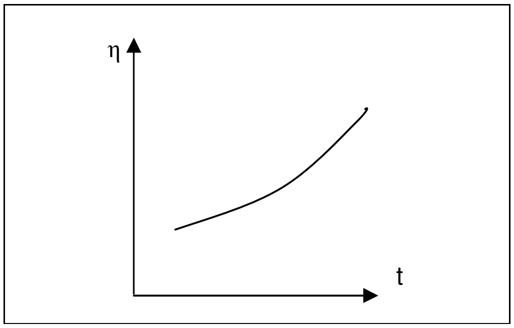

Figure 4. Flow curve of rheopexy

Both thixotrophy and rheopexy may occur in combination with any other flow behaviours, or only at certain shear rates. The time element is extremely variable; under conditions of constant shear, some fluids will reach their final viscosity value in seconds, while others may take up to several days. Rheopectic fluids are rarely encountered. Thixotrophy, however, is frequently observed in materials such as greases, heavy printing inks, and paints. Thixotropy usually occurs in circumstances where the liquid is shear-thinning; in the sense that viscosity levels decrease with increasing shear rate, other things being equal (Barnes et al., 1989).

2.2.2 Time Independent non-Newtonian fluids

2.2.2.1 Pseudoplastic

This type of fluid will display a decreasing viscosity with an increasing shear rate as shown in Figure 5.

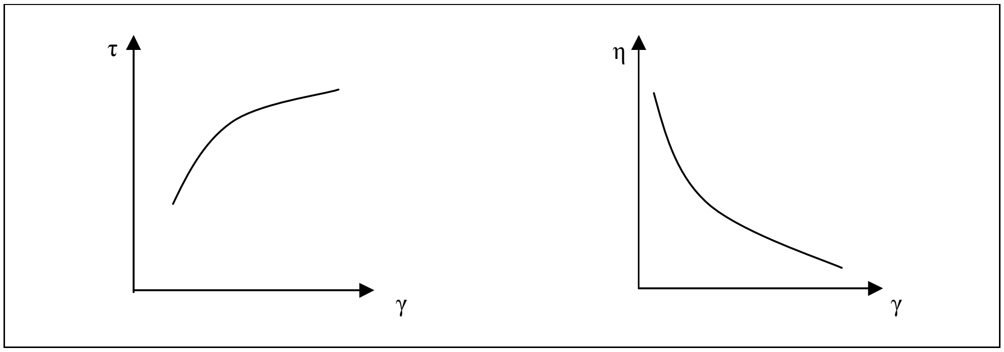

Figure 5. Flow curves for non-newtonian fluids

The most common of the non-Newtonian fluids, pseudo-plastics include paints, emulsions, and dispersions of many types. This type of flow behavior is sometimes called "shear-thinning". An easily understanding model is to imagine that in the moment of turning the spindle in the sample the structure of molecules of the sample will be destroyed, and the molecule formation will be oriented more parallel to the spindle surface. So the hindering of the spindle rotation will increase. The faster the rotation will become, the more the structure is destroyed and the less the structure of molecules slide in together, the lower the viscosity will be (Brookfield Catalog).

2.2.2.2 Dilatant

Increasing viscosity with an increase in shear rate characterizes the dilatant fluid as shown in Figure 6.

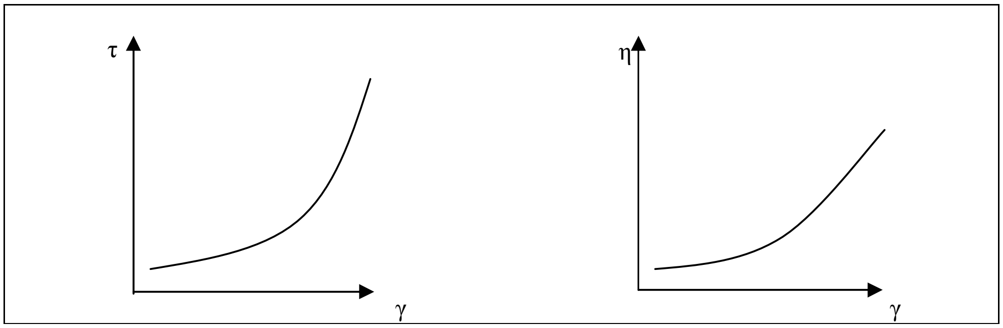

Figure 6. Flow curves for dilatant fluids

Dilatancy is frequently observed in fluids containing high levels of deflocculated solids, such as clay slurries, candy compounds.

2.2.2.3 Plastic

This type of fluid will behave as a solid under static conditions. A certain amount of stress must be applied to the fluid before any flow is induced; this stress is called the "yield stress". Tomato catsup is a good example of this type fluid. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic, or dilatant characteristics.

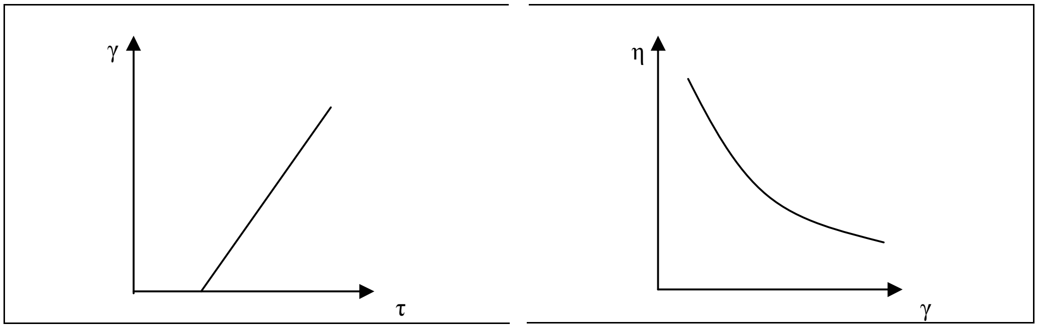

Figure 7. Flow curves for plastic fluid

CHAPTER 3

COAL-WATER MIXTURES

3.1 Background

Coal-liquid mixtures consist of finely ground coal suspended in a liquid, such as oil or water, together with small amounts of chemical additives to improve stability, homogeneity and dispersibility. The primary purpose of coal-liquid mixtures is to make solid coal behave as an essentially liquid fuel that can be transported, stored, and burned in a manner similar to heavy fuel oil. The most mature coal-liquid mixture technologies are those using coal-oil and coal-water mixtures (CWM). Several of these technologies already have been offered commercially. Since coal-liquid mixtures are intended as an alternative for oil, their market penetration will be probably being dependent on oil prices (Coal Energy for the Future, 1995).

3.2 Development History

Initial development work on coal-oil mixtures (COM) dates back to the last century. Extensive COM research was conducted in the United States during the 1940s because of wartime constraints on oil supply. More recent interest in COMs followed the 1974 OPEC oil embargo and the oil price hikes of late 1970s. Utility and industrial boiler demonstrations using COMs were conducted in the United States, Japan, Sweden, and England between 1977 and 1981. Over 20 COM preparation plants are currently operating or have been operated in various countries.

The first combustion tests of CWMs -also known as coal-water slurries (CMSs) - were conducted in the United States, Germany, and the Soviet Union in the 1960s.

There was active development of CWMs in the United States in the 1980s, with emphasis on developing technologies to prepare mixtures with desirable physical and chemical properties, demonstrating retrofit in existing boilers, and developing specialized equipment for handling and transporting slurries. During this period, a number of private companies were actively involved in, or abandoned commercialization of slurries as oil prices declined in the early 1980s (Coal Energy for the Future, 1995).

Early efforts in CWM technology development mainly concentrated on the preparation of high energy concentrated on the preparation of high energy density liquid fuel from bituminous coals. The first attempts to utilize low rank coals (LRC) for this purpose consisted of simply mixing the pulverized LRC in its natural state directly with water. Chemical additives were not used and no changes were made to its surface characteristics. The result was that the utilization of LRC in its natural state was not economically feasible due to its extremely low energy content and unfavorable characteristics before and after burning (Witsee et al., 1986). However the recent introduction of chemical additives has made LRC utilization as CWMs possible and feasible (Uyar et al., 1994)

The particle size distribution of the ground coal must be approximately adjusted to allow high solids loading of the CWM, and the chemical additives should match the interfacial properties of the coal particles, to lower the CWM viscosity and increase its stability. CWM with such properties behaves as a liquid fuel: it is pumpable, can be atomized using a specially designed nozzle, ignited in a preheated environment, and hence stably combusted in a boiler or furnace (Wang et al., 1993).

Ideal CWM with maximum coal loading should be relatively stable at static state and during transportation, and exhibit good rheological behaviour. Rheological behaviour affects the atomization of CWM, which will influence the combustibility of CWM in boiler application. (Li and Li, 2000) The industrially expected value for the viscosity of a CWM, even though not absolute, is Brookfield apparent viscosity of 1000 cp at 100 rpm. (Natoli et al., 1985)

3.3. Application Areas of Coal-Water Mixtures

The application areas of coal-water mixtures can be summarized as in Table 1.

Table 1. Application Areas of Coal-Water Mixtures (Bognolo, 1987)

Application Area	**Application Strategy**	**Required Property**
Industrial establishments Regional heating Electric or heat production for greenhouse	* Production of CWM in a central place * Distribution by overland or seaway * Storage and combustion at consumption area	* Loading 70% coal by weight * Stability of mixtures, in static and dynamic conditions, enough time * Efficient combustion property * Suitability for environment
Industrial establishments Power plants	* Preparation of CWM in the production region of coal * Distribution with pipeline * Storage and combustion at the place where the coal is transported	* Coal loading providing efficient combustion * Combustion property * Suitability for environment
Steel industry	Additive to high furnace fuel	* High loading coal *Dynamic stability, minimum storage stability
Coal liquidification/ gasification	Coal mixtures	* High loading coal * Dynamic stability although its little
Fuel	Diesel engine fuel	* High loading coal * Good rheology under the conditions of small particle size and high loading coal * Combustion without any problem * Mixtures without ash

3.4 Industrial Applications

3.4.1 China

China is rich in coal resources but lacks of petroleum. Meanwhile, about a third of petroleum produced is burnt away as fuel. Thus, CWM as a new coal fuel and substitute for oil has been a key R & D project in China since 1980's. Five CWM plants constructed with an annual capacity of 85 000 ton. CWM has been successfully tested and operated in various boilers for power generation and petroleum, petrochemistry, chemical and metallurgical industries. During the development of CWM, it has been found that the stability of CWM of some of the coals is too low, which has limited the application of CWM. (Li and Li, 2000)

7 million ton/year capacity of pipeline has established in Shaanxi coal area. One of the CWMs with approximately 5.6 million ton capacity reached to Xincheng which is 338 km away and another one reached to Dagang which is 853 km away. Coal extracted in Area Yanzhou of China transferred to Area Rizhou via railway which is 300 km away. CWM production takes place there with capacity 250 000 ton/year. Afterwards, it is transported with tankers 1100 km to Japan-Wakamatsu and stored there. This product is brought to the user in Okayama area which is 400 km away via sea transportation through the shoreline (Yavuz and Küçükbayrak, 1998).

3.4.2 Russia

Russia has positive experience in production, transportation and combustion of CWMs. After being prepared by Ugleprovod in Belovo, a CWM was supplied through a 298 km long pipeline to the heat power station No.5 in Novosibirsk. The solid fraction (62%) is the coal from Inskaya mine in Belovo city. The dispersed media is water (37%), and the rest 1% is a plastificizer- sulfate salts of naphthalene-formaldehyde with surfactant properties (the admixture C-3). The solid phase of the CWM has a grain size range 20-350 μm. The technology specification for the CWM supplied to boilers dictated the level of viscosity at about 800 centipoises. (Burdukov et al, 2002)

3.4.3 USA

In USA, studies for atomizing and burning of CWM fuel in commercial sizes have been continuing since 1980. Burning of fuel has been processed in many plants. In 1983, a thirty five days test carried out at E.I.du Pont de Nemours&Co. in Memphis showed that CWMs can be used safely. In 1985, B&W and Ashland Oil Co., had a test at nuclear supplies unit. US Fluidcarbon Inc. supplied the necessary CWM to Carolina Electric and Gas Utilities Division for testing of CWM at 75 MWe coal ignition boilers. The goal was to experience the long-term use of the fuel. The mixture was obtained as planned and the boiler was operated successfully (Yavuz and Küçükbayrak, 1998).

3.4.4 Canada

The first important CWM test was started in 1982 with the cooperation between The New Brunswick Electric Power Comission and Cape Breton Development Cormporation (CBDC) in order to produce CWM and the use of this fuel in two boilers which were designed for coal.

The units at Catham, New Brunswick had capacities of 12 and 20 MWe. The mixtures were obtained from a plant in Sidney, Nova Scotia. The successful results let the program continue. The market research showed that there is a substantial potential for the use of CWM in East Canada. Especially industrial users like pulp and paper industry are defined sectors to benefit from this new fuel technology. In 1984 and 1985, Canada Cement LeFarge Ltd, has converted their two burning furnaces which were used for cement production to CWM. The first burning test has started in 1984 and as a result of this test CWM was accepted as primary fuel for the plant. The use of CWM still continues (Yavuz and Küçükbayrak, 1998).

3.4.5 Sweden

CWMs were tested in various boilers in Sweden. Svenska Fluidcarbon has supplied the required fuel for three boilers with capacities of 10 MWe (two) and 6 MWe. CWM was used in a regional heating system for 2000 hours in Sundyberg. In the operation period which covers three heating period, it was proven that CWM could be used as an alternative fuel for boilers. Svenska Fluidcarbon made three contracts in Switzerland. At the end of a succesful and long term test (from 1983 to May 1985) Energy Utility of Lund, had the conversion of boilers and signed a contract for the distribution of fuel for seven years with Svenska Fluidcarbon on December 1984. A 29 MWe boiler has supplied steam and hot water for regional heating system for the university hospital. The second agreement was made with KF/Foodia AB which is a food processing plant in Staffanstorp, outside of Malmö. The Svenska Fluidcarbon contract includes the conversion of the operation and the fuel supply for seven years. The third commercial agreement was done with SABNIFE plant in Osbarshamn, which is the manufacturer of Fe-Ni batteries (Yavuz and Küçükbayrak, 1998).

CHAPTER 4

PREVIOUS STUDIES ABOUT COAL-WATER MIXTURES

CWM, as non-Newtonian fluids, should possess the characteristic of an apparent viscosity function that decrease with the increasing shear rate. Pseudoplastic fluids exhibit such "shear thinning" behavior without yield stress. Dilatant fluids, on the contrary exhibit shear-thickening behaviour. Expensive additives, dispersants and stabilizers have usually been used to improve the rheological behavior and the static stability of CWM to meet the requirement of its transportation, storage and combustion in industrial application (Sun Chu-G et al., 1995).

The rheology of the coal suspension depends on the interparticle attractive forces; these in turn depend on the chemical structure of the surface, which is specific to a particular coal and total surface area, which can be inferred from its concentration in the suspension and the particle size distribution. Inherent in a specific coal is its porosity which may affect the adsorption of the reagents but which may be supposed to contribute to the interparticle attraction. The interparticle forces can be modified by the presence in the suspension water of surface-active chemicals, inorganic electrolytes, pH and polyelectrolytes (Aktaş and Woodburn, 2000).

Viscosity that affects the fluidity of the CWM primarily depends on the coal properties and there is a delicate balance between the viscosity, fluidity and the settlement rate of the particles (Ateşok et al., 2002). The industrially expected value for the viscosity of a CWM, even though not absolute, is Brookfield apparent viscosity of 1000 cp at 100 rpm (Natoli et al., 1985).

The surface charge of the coal particle changes with coal structure, and it can be controlled by employing chemical additives. When the surface charge is low, particles agglomerate and viscosity increases. The opposite is valid when the surface charge is high. For good settling stability and low viscosity, an optimum level can be achieved for each coal type (Beer, 1985). Atlas et al. (1985) has been summarized the relationship between surface charge and properties of mixtures as in Figure 8.

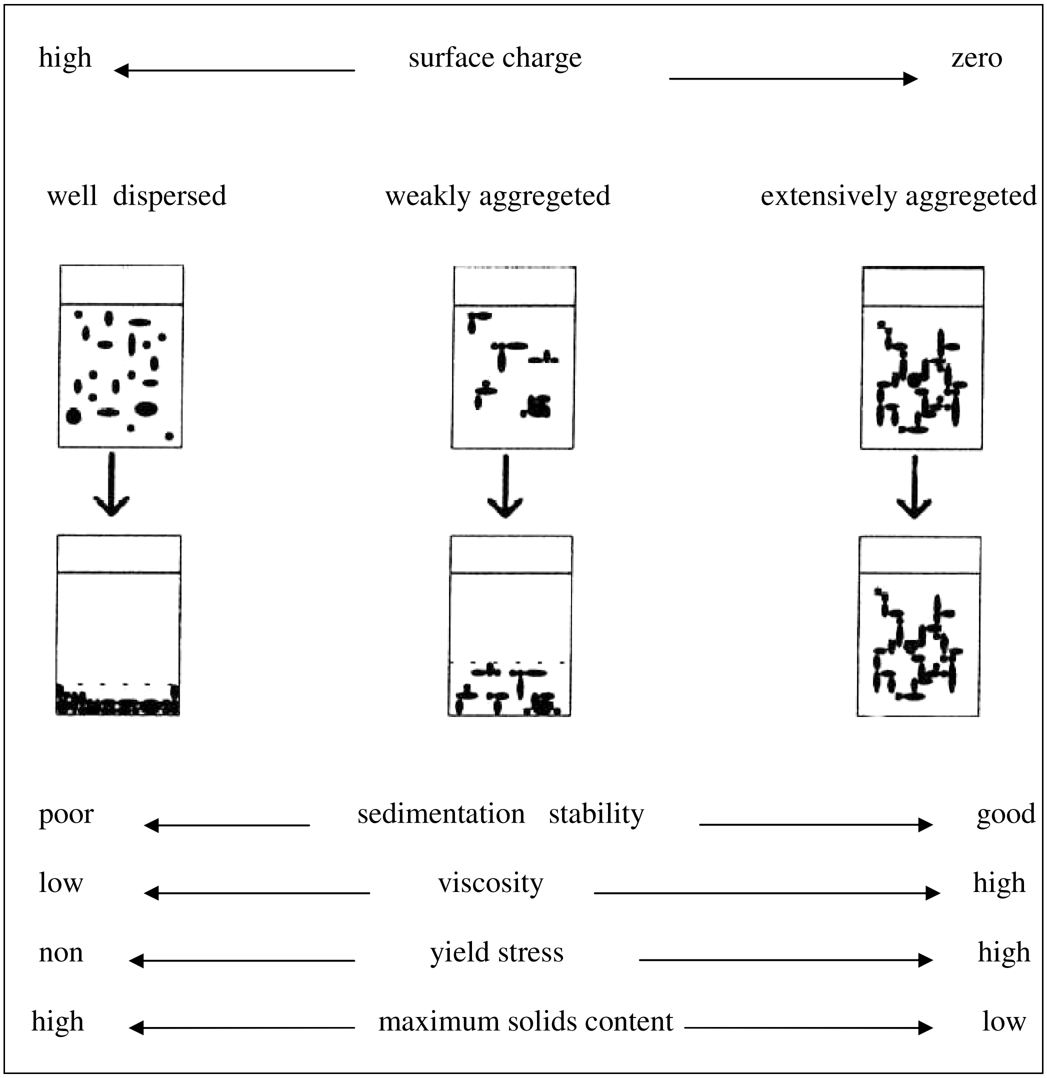

Figure 8. Illustration of particle suspensions showing that at a given solid content the volume of sediment depends on particle aggregation (Atlas et al., 1985).

The rheological properties of CWM depend on a number of factors such as the type of coal, the solid concentration and its size distribution, the temperature, the pulp pH and the presence of electrolytes and chemical additives.

4.1. Effect of Type of Coal on CWM

The following factors related to physical-chemical properties of coal dominantly influence the fluidity and stability of CWM:

i) the moisture and ash contents of coal
ii) the organic factors: oxygen/carbon ratio (O/C) and oxygen-containing functional groups: hydroxyl oxygen (O_{OH}) and carboxyl oxygen (O_{COOH}) . (Tiwari et al., 2003)

The coal containing relatively more ash may lead to form strong aggregation and gel state at high coal loadings resulting in increase in the viscosity of CWM (Tiwari et al., 2003). Aktaş and Woodburn (2000) observed that the viscosities of the slurries with low ash content were significantly reduced by the surfactant addition which also altered the rheological characters of these slurries from non-Newtonian towards Newtonian fluids. However sample containing very fine particles with a high ash content showed non-Newtonian behaviour even in the presence of reagent.

The content of moisture, oxygen containing functional groups of $O_{OH,}$ O_{COOH} and O/C ratios of coals influence the hydrophilic character of coal. The more hydrophilic coal is likely to hold the greater deal of water. Hence, coal having relatively lower moisture and oxygen containing groups would make the more highly loaded CWM because of its higher hydrophobicity (Tiwari et al., 2003, Kanamori et al., 1990, Shuguan and Zuna, 1990).

Taweel and Fadaly (1985) concluded that as O/C and H/C ratios of the coal increase so does the surface activity, therefore the coal can readily adsorb chemical additives. On the other hand, bituminous coals with lower O/C ratios cause better fluidity compared to younger coals with higher O/C ratios (Wu J. et al., 1961).

Boger et al. (1987) proposed that as the coal rank decreased substantial increases in the apparent viscosity were observed. In order to prepare CWMs with high solids content using low rank coals, the coal should have low porosity and highly be hydrophobic (Leong et al., 1993, Skolnik and Scheffee, 1985).

4.2. Effect of Particle Size Distribution

The particle size distribution is one of the most important variables in the preparation of a coal-water mixture. The viscosity of a coal-water mixture can be reduced to a minimum value by optimizing its particle size distribution. Further reduction via viscosity can only be attained by the use of chemical additives (Boylu et al., 2003).

It has been determined that the particle diameter of fine coal used in the preparation of CWM should be a maximum of 250 μm (Allen, 1984). It has also been indicated that generally 70-80 % of particles should have a diameter less than 74 μm and a mean particle diameter between 20-30 μm.

In suspension rheology, solid concentrations are expressed as volume fraction. Volume fraction is such a parameter that depends on the solids particle size distribution and particle shape. The volume fraction is defined as the ratio of the volume of a known amount of particles after vibrating in a graduated cylinder for a certain period of time to the initial bulk volume. According to Boylu et al. (2003), CWM in which the particle size distribution is adjusted to give the maximum packing fraction has better rheological properties in the sense that the apparent viscosities are low; and it was observed that in the case of a wide range of particle size distribution, fine particles fill the gaps between coarse particles and therefore higher volume fractions.

Toda et al. (1988) observed that a distribution of particle sizes which gives maximum volume fraction is desirable to obtain a CWM with low viscosity. Yavuz (1996) determined that slurries containing fine particles have high viscosities and low volume fraction.

Logos and Nguyen (1996) observed that, slurries containing only fine particles exhibit a wide spectrum of flow behaviour ranging from Newtonian as low solid concentrations to shear-thinning and viscoplastic with a yield stress at higher concentration and Aktaş and Woodburn(2000) observed that very fine coal particles containing high ash content showed non-Newtonian behaviour even in the presence of reagent.

Keller and Keller (1991) suggested that when the particle size range increased, the viscosity values dropped at low shear rates because of the decrease in Brownian movements. Roh et al (1995), and Logos and Nguyen (1996) used mixing of coarse and fine coal particles and found very effective in obtaining mixtures characterized by low viscosity with high solid loadings.

4.3. Effect of Chemical Additives used in CWM

The surface charge of the coal particle changes with coal structure, and it can be controlled by employing chemical additives. When selecting an additive, possible counter effect on emission (sulphur or nitrogen compounds), slagging and corrosion (sodium and similar salts) should also be considered (Hammond and Beckhusen, 1986).

Viscosity measurements showed that surfactant addition to the suspension affected the rheology. This is presumed to be related to the adsorption of the reagent on the coal surface, which is dependent both on the nature of the surface and the reagent type and its concentration (Charpman and Lynch, 1986).

Chemical additives used in CWMs are dispersing agents to reduce viscosity and stabilizers to reduce settling. Boylu et al (2003) used Sodium Polystyrene Sulphonate (PSS), as dispersing agent and Sodium salt of carboxymethyl cellulose (CMC-Na) as stabilizer in their studies. Amount of chemical agents used was selected to be 1% by weight of solids of which consisted of 90% PSS and 10% was Na-CMC.

Aktaş and Woodburn (2000) used Triton X-405 non ionic surfactant and concluded that to produce pumpable slurries with more than 60% solid, it will be necessary first to achieve a significant level of demineralization, and to use high levels of reagent addition.

Ateşok et al (2002) concluded that the addition of chemical additives is necessary to increase the absolute value of zeta potential to sustain stability and Funk (1981) found that high value of zeta potential led to minimum viscosity and good dispersion.

Tiwari et al. (2003) studied the effect of two newly developed anionic additives in the formation of CWM (One naphthalene-based and the other naphthalene-tolune-based).

4.4. Effect of Pulp Density

Investigations shows that the rheological behavior of CWM, changes from a fluid exhibiting the properties of a low viscosity Newtonian fluid at low concentrations, to a fluid with the properties of high viscosity non-Newtonian pseudoplastic (Aktaş and Woodburn, 2000).

Non-linear rheological behaviour occurs at high concentrations for suspensions comprised of narrow sized fractions of spherical particles, and that these effects arise at lower concentrations for non-spherical particles and/or for suspensions comprised of even spherical particles of broad particle size distributions (Turian et al., 2002).

The presence of water in CWM naturally decreases the overall efficiency of the boiler. However, this decrease is minimal and estimated to be around 1% for each 10% of water contained with CWM (Beer, 1985)

4.5. Effect of pH

Rheological properties of CWM depend on the pH value and zeta potential. Yavuz (1996) resulted that dispersant adsorption efficiency of Pellupur B69 was higher at pH< 7 for all the lignite samples studied and for Tween-80 this was changed depending on the nature of the lignite sample. Kütahya-Gediz lignite sample showed the best adsorption behaviour at neutral pH.

Turian et al. (1992) suggested that yield stress of CWM is highest at low pH and decreases progressively with increasing pH. The (negative value of) zeta potential increases with increasing pH, with a corresponding recovery of the repulsive component in particle interactions. At low pH (high hydrogen ion concentration in the supernatant) the surface charge is low as the functional groups are hydrogen-ion exchanged into the free acid form. Therefore, the net interaction between particles is attractive and leads to flocculation. The higher values of the yield stress of CWM corresponding to the relatively more flocculated states prevailing at the lower pH values (Street, N., 1956, Turian et al., 1992).

Hiçyılmaz et al. (2006) observed that the viscosity decreases at alkaline conditions because of the higher negative surface potential of asphaltite particles under the effect of an increased OH^- ion concentration in the slurry. Özdemir (1997), found the lowest viscosity value (CWM with Zonguldak coal) when the pH was 7.9.

CHAPTER 5

EXPERIMENTAL STUDIES

35 kg of run of mine coal samples were brought to mineral processing laboratories of METU Mining Engineering Department from Park Energy Çayırhan Mining Plant.

The large coal pieces were first crushed by a hammer; after that the coal samples were divided into two representative pieces. One of them was packed in order to prevent oxidation. The other representative half was crushed by a jaw crusher, and then the crushed coal was screened through -9.53 mm sieve. The undersize coal was collected and the oversize coal was recrushed to get all coal particle size -9.53 mm. The -9.53 mm coal was divided representatively into 250 grams portions with riffle and packaged with plastic bags to prevent oxidation.

5.1 Çayırhan Lignite Sample

Proximate and Ultimate Analyses were done to characterize the coal sample. Table 2 shows the proximate analyses and Table 3 shows the ultimate analyses of sample, respectively.

Table 2. Proximate Analyses of Çayırhan Lignite Sample

Proximate Analysis (as received)	
Moisture (wt %)	17.04
Ash (wt %)	48.28
Volatile matter (wt %)	25.89
Fixed Carbon (wt %)	8.79
Total	100

Table 3. Ultimate Analyses of Çayırhan Lignite Sample

Ultimate Analysis (air dried)	
C (wt %)	20.39
H (wt %)	1.59
N (wt %)	0.55
S (wt %)	1.20
O (wt %)	10.96
Sulfur (total) (wt %)	2.72
Lower calorific value (Kcal/kg)	1684
Higher calorific value (Kcal/ kg)	1891

Proximate analyses were done in METU Mining Engineering Department Laboratories according to ASTM Standards while the Ultimate analyses were done in MTA.

5.2 Particle Size Analyses of Lignite Samples

250 g coal sample were dry ground for 5, 10 and 15 minutes with 19.3 Φ × 30.3 cm laboratory type rod mill with 28 cm rods (2 × 37.7 mm Φ, 5 × 23.9 mm Φ and 8 × 16.6 mm Φ).

Figure 9 shows the Laboratory type rod mill used through the experiments research.

Size distribution of samples were determined with Symtatec Laser Seizer (Helas (H1305)) The size distributions of the samples were given in Figure 10 and Table 4 shows the d_{50} , d_{80} and arithmetic mean sizes of the ground samples.

Figure 9. Laboratory type rod mill

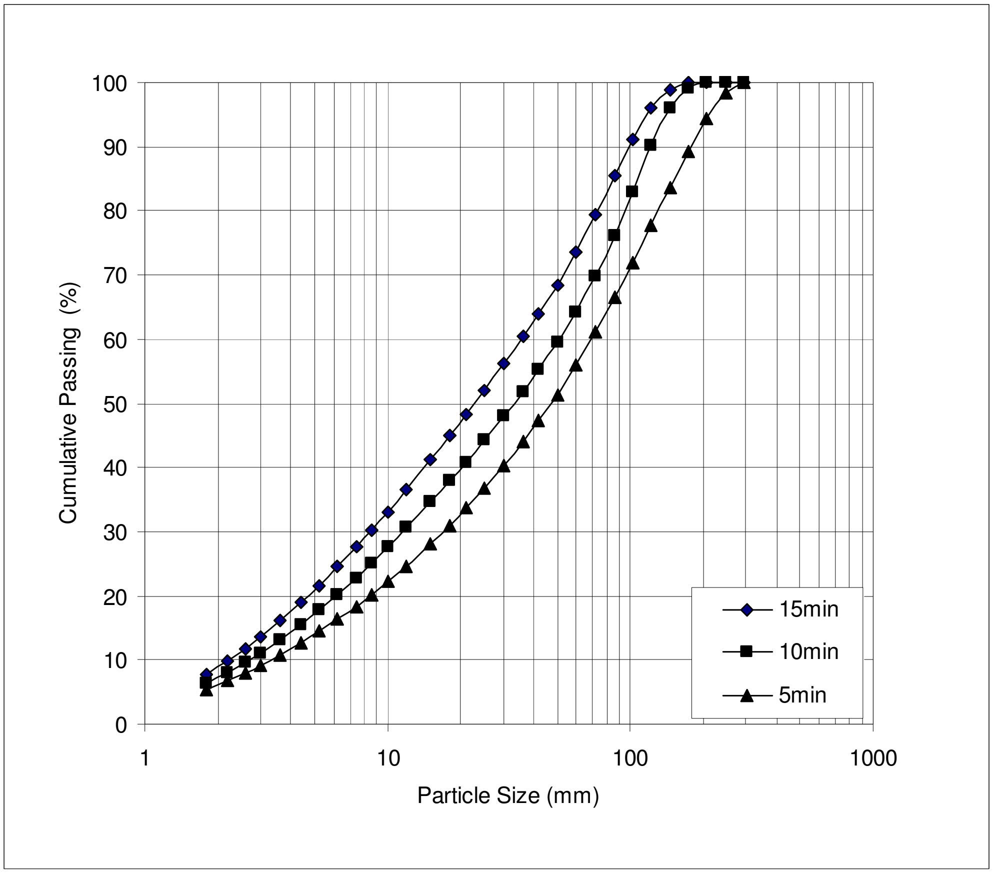

Figure 10. Particle Size Distributions of Lignite Samples

Table 4. Maximum particle size, d_{50}, d_{80} and arithmetic mean of 5, 10, 15 minutes ground lignite samples

Grinding time (minute)	Maximum particle size(µm)	d_{50} (µm)	Arithmetic mean (µm)	d_{80} (µm)
5	294	47.42	70.6	120
10	206	33	49.91	93
15	174	22.82	38.43	73

In the experiments, 15 minutes ground coal (d_{50}=22.82 μm) was preferred at the beginning. After grinding, the samples were dried using laboratory type furnace at least three days at 47±1 ^{o}C to control the moisture content of coal throughout the experiments.

5.3. Chemical Agents used in Experiments

Two chemicals were used, namely Polystyrene Sulphonate (PSS) as dispersant (90%) and Sodium Carboxymethyl cellulose (Na-CMC) as stabilizer (10%). The research was carried on with 1% chemical agent by weight at the beginning of experiments. The effect of chemical amount was tested as mentioned before.

The physical properties and the chemical structures of PSS and Na-CMC are as follows;

5.3.1. Na-CMC

Na-CMC is a completely water-soluble polymer, not an ion exchanger and has low viscosity.
Synonym: Sodium Carboxymethylcellulose
Figure 11 shows the chemical structure of Na-CMC.

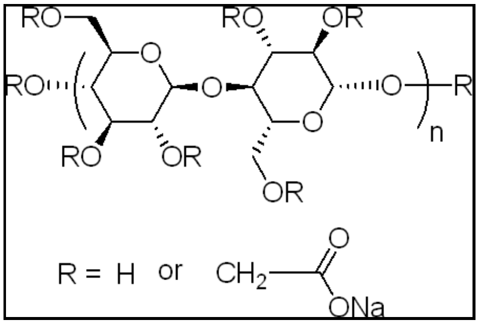

Figure.11. Chemical Structure of Na-CMC (Sigma Catalog)

A stock solution was prepared in the form of 2.5% solution by weight and then this stock solution was used throughout the research.

5.3.2. PSS

Synonym: PEDOT/PSS
Poly (3, 4-oxyethyleneoxythiophene)/poly (styrene sulfonate)
Poly (styrenesulfonate)/poly (2, 3-dihydrothieno [3, 4-b]-1, 4-dioxin)

Figure 12 shows the chemical structure of PSS.

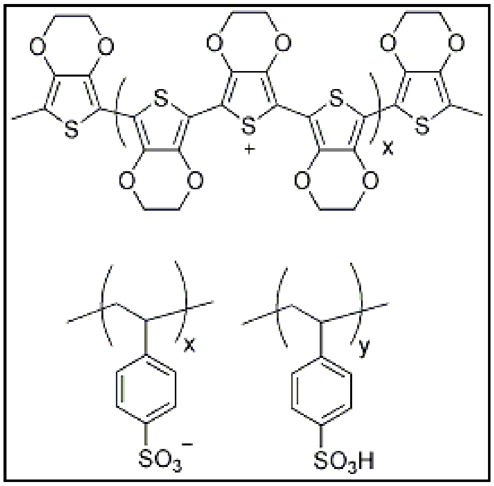

Figure.12. Chemical Structure of PSS (Sigma Catalog)

5.4 Viscometer

The experiments were performed by using RVDV-II +Pro Model Brookfield rotating viscometer with a SC4-27 type spindle which measures fluid viscosity at given shear rates. When the shear rate is varied, the shear stress does not vary in the same proportion depending on the type of fluid. The viscosity of fluids change as the shear rate is varied. The experimental parameters of Viscometer model, spindle and speed all have an effect on the measured viscosity of a non-Newtonian fluid. This measured viscosity is called the “apparent viscosity” of fluid. In this thesis, the word viscosity represents the “apparent viscosity”.

The relationship between the viscosity, shear rate and shear stress is as follows;

$\gamma = SRC \times n$

$\tau = VTC \times SMC \times SRC \times T$

$\eta = (100/n) \times VTC \times SRC \times T$

where; SRC: shear rate constant (0.34 for the used instrument)
n: rotational speed (rpm)
VTC: viscosity torque constant (1.0 for the used instrument)
SMC: spindle multiplier constant (25 for the used instrument)
T : torque (dyne cm^{-2})
γ: shear rate (s^{-1})
τ: shear stress (dyne cm^{-2} or centipoises s^{-1})
η: viscosity (centipoises)

Shear rate constant is multiplied by the Viscometer's rotational speed (in RPM) to obtain the shear rate (in reciprocals seconds) for that speed. The constants are independent of Viscometer model, sample viscosity, or temperature.

Spindle Factors are constants related to Viscometers rotational speed. Spindle Factors are traditionally used to convert the torque value on a Dial Reading Viscometer to a centipoises value. Divide the given constant by the speed in use to obtain the Spindle Factor for that spindle/speed combination. The Spindle factor is then multiplied by the Viscometer's dial reading to obtain viscosity (in centipoises).

The spindle factor for SC4-27 spindle with 13R chamber on an RV Viscometer is 2500/N. At 100 rpm, the spindle factor is 2500/100. Multiplying all dial viscometer readings made with this spindle/speed combination by 25 gives viscosity in centipoises.

5.4.1. Coni-Cylindirical Viscometer Cell

Figure 13 shows a schematic view of a coni-cylindirical viscometer cell. Several commercially available instruments have used modifications of this design. The advantage of the combined coaxial cylinder and conical viscometer is that the mean rate of shear in the cylindrical annulus and in the conical portion is about the same and the end effect is nearly eliminated. (Wazer et al, 1963)

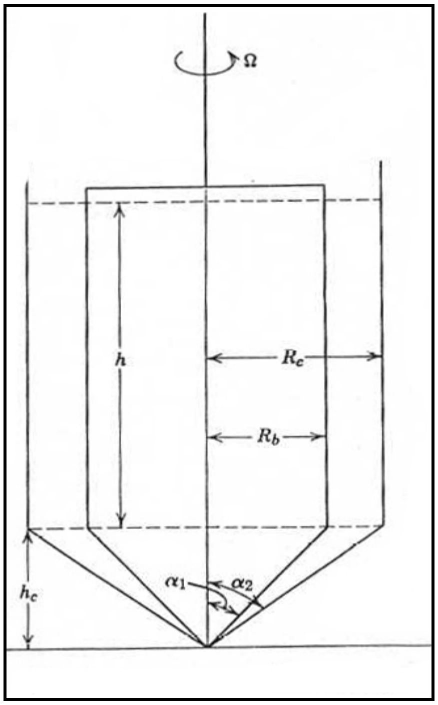

Figure 13. Coni-cylindirical viscometer cell. (Wazer et al, 1963)

where; R_c : Radius of chamber
R_b : Radius of spindle
α_1 : Spindle cone angle
α_2 : Chamber cone angle
Ω : Angular velocity of spindle

Figure 14. Brookfield RVDV-II model Viscometer with SC4-27 type spindle

5.5 Method

First, necessary amount of distilled water, PSS and CMC were added into a 250 ml volume beaker respectively and mixed. Then, Junke&Kunkel (Ika Labortecknik) RW 20 model mixer with 5.4 cm impeller (Figure 15) was used to mix coal and liquid. Necessary amount of coal was fed at 300 rpm through 5 minutes. After the addition of all coal samples, the CWM was mixed for 15 minutes at 1000 rpm. The total volume of CWM (90 ml) in beaker was kept constant in all experiments to standardize the mixing. At the end of the mixing, about 4 ml of CWM was used for measuring viscosities by using Brookfield RVDV-II model Viscometer with SC4-27 type spindle. In Appendix, Tables A.1 to A.6 show the amounts of coal, water and chemical agents used in each experiment.

Experiments were conducted at 100 rpm and 34 sec^{-1} shear rate and totally 1% chemical agent (10% Na-CMC, 90% PSS) by weight was used initially. pH of the mixture was adjusted by HCl or NaOH (in the form of 10% solutions) in the case of necessity and pH was measured by using pH meter.

Two programs were prepared and downloaded to viscometer. First, at constant shear rate, changing in viscosities were measured through 16 minutes and results were taken at 30 seconds intervals. These data showed the character of fluid. After this experiments, second program was run and the effect of changing in rotational speed on viscosity was observed to understand the mixtures were whether shear-thinning or shear-thickening. Rotational speed was changed to 50, 100, 150 and 200 rpm.

5.6. Zeta Potential Measurement

Zeta Potential Measurements were carried out with instrument Malvern Zetasizer Nano-Z. Coal was prepared for the measurement. First, coal leached with HCl. The addition of HCl was continued until the leaching of carbonate minerals was stopped. Then, coal washed with distilled water several times until the filtrate became clean (neutral pH and colourless). Finally, the clean coal was dried in furnace at 47 ±2 ^{o}C and a solution was prepared for zeta potential measurement.

Figure 15. Junke&Kunkel RW 20 model mixer with 5.4 cm impeller

CHAPTER 6

RESULTS AND DISCUSSION

The rheological behaviour of Çayırhan CWMs as a function of the concerned parameters was presented from four view points. Firstly the viscosity was evaluated as a function of time. The viscosity profiles were drawn over a certain time period and the rheological characteristics were determined from the view of Newtonian or non-Newtonian together with thioxotrophic or rheopectic behaviour. Then, the viscosity values achieved at the 570th second of measurement were presented and compared in the form of graph. Thirdly, shear stress vs. shear rate profiles were drawn which confirm the character of fluid as a Newtonian or non-Newtonian. Lastly, the viscosity changes as a function of shear rate was drawn to determine whether it is shear-thinning or shear-thickening.

6.1 Effect of Pulp Density

In this study, experiments were performed to determine the applicable maximum pulp density and to observe the behaviour of viscosity against pulp density. Experiments were conducted at 100 rpm and 34 sec^{-1} shear rate and totally 1% chemical agent (10% Na-CMC, 90% PSS) by weight was used.

It is desirable to have high solid contents in CWM. Critical solid content (CSC) is reached when the volume of liquid phase equals the void volume of the solid phase. As the CSC limit is approached, the viscosity of CWM increases sharply. At the CSC, there is no extra liquid left between the particles under this condition (Uyar et al, 1994). In heavily loaded suspensions, aggregation creates a network of interacting particles and sharply increases the viscosity (Laskowski, 2001).

The testing of effect of pulp density was started from the value of 54% solid by weight up to approaching to CSC. The solid % by weight was changed with 2% increment. Therefore the experiments were carried out at 54, 56, 58, 60 and 62% solid by weight. The results are shown in Figures 16, 17, 18 and 19. As it seen from Figures 16 and 17, the viscosity values increased with the increasing of pulp density. 62% pulp density was the maximum value, that mixing and viscosity measurement could be performed. Therefore, 62% pulp density is the upper limit to perform the experiments. Above 62% pulp density mixing of coal, water and chemicals could not be done effectively. So that higher pulp densities was not tested.

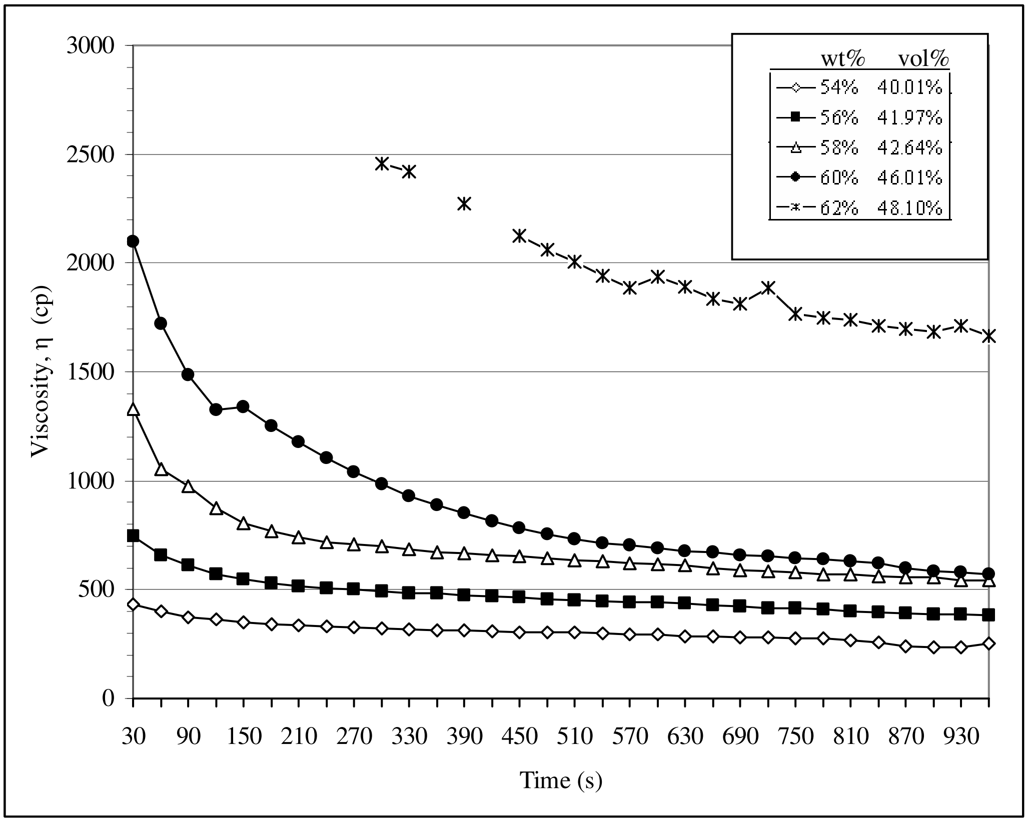

Figure 16. Effect of Pulp Density on Viscosity of CWM.

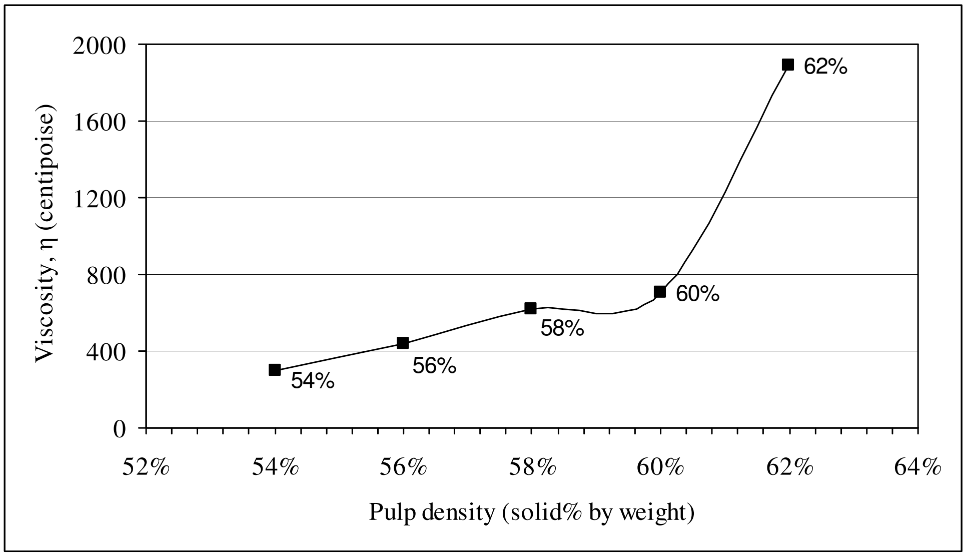

Figure 17. Change of viscosity as a function of the CWM pulp density at the 570th second.

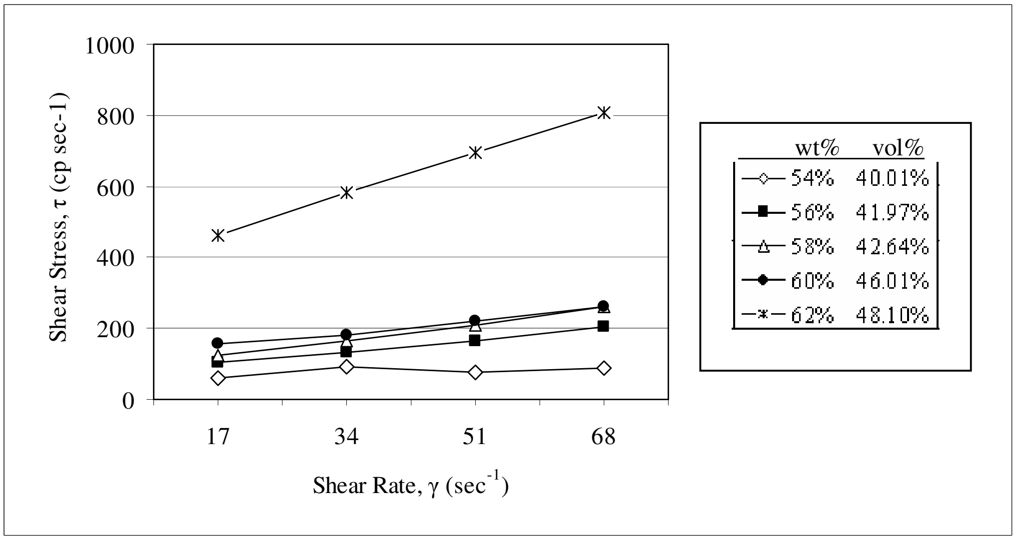

Figure 18. Shear Rate vs. Shear Stress for Different Pulp Densities of CWMs.

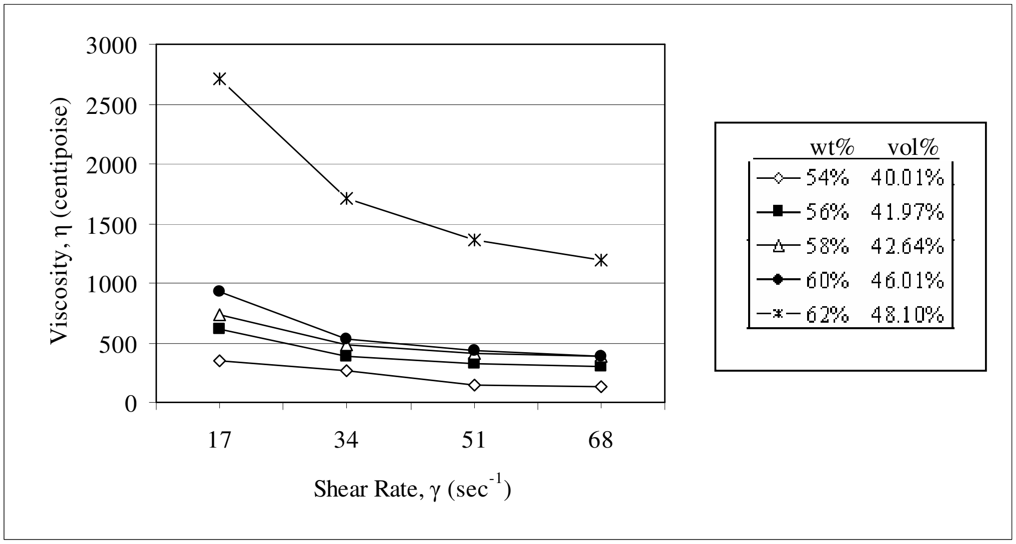

Figure 19. Shear Rate vs. Viscosity for Different Pulp Densities of CWMs

However, at 60% pulp density, the mixing could be done effectively and the viscosity measurements were taken regularly; therefore 60% pulp density is the CSC limit. Since the purpose was to obtain maximum coal loading to increase efficiency and economy, 60% pulp density was chosen for the following experiments.

The results that can be observed from the figures 16 and 18 are about the rheological character of CWM. As seen from Figure 16, the viscosity of mixtures decreases with time which means that CWM is thixotrophic non-Newtonian fluid. On the other hand, as the pulp density decreases, the liquid behaviour closes to Newtonian fluid character. In lowest pulp density, significant reduction can not be observed, and only in first minutes the viscosity changes with a very low reduction. However it can not be said that it is Newtonian.

From Figures 18 and 19, it is seen that mixtures display a decreasing viscosity and increasing shear stress with an increasing shear rate. These properties show that the mixtures are non-Newtonian, shear-thinning.

6.2. Effect of Amount of Chemical Agents

The surface charge of the coal particle changes with coal structure, and it can be controlled by employing chemical additives. When the surface charge is low, particles can agglomerate and viscosity increases. The opposite is valid when the surface charge is high. For good dispersing stability and low viscosity, an optimum level of chemical agent can be achieved for each coal type (Beer, 1985).

In these experiments, the amount of total chemical agents which were used for stability and dispersibility was changed and their effects on viscosity were investigated. As a dispersant agent polystyrene sulfonate (PSS) and as stabilizer agent sodium carboxymethyl cellulose (Na-CMC), were used. The ratio of PSS/CMC (9:1) was kept constant and total amount of chemical was changed from 0% to 1.4%.

The results of experiments are given in Figures 20, 21, 22 and 23. As it is seen, at all dosages, CWMs had a non-Newtonian flow character. Also, at all dosages CWMs preserved their “thioxotrophic” (the viscosity of CWMs tended to decrease with time) and shear-thinning behaviour.

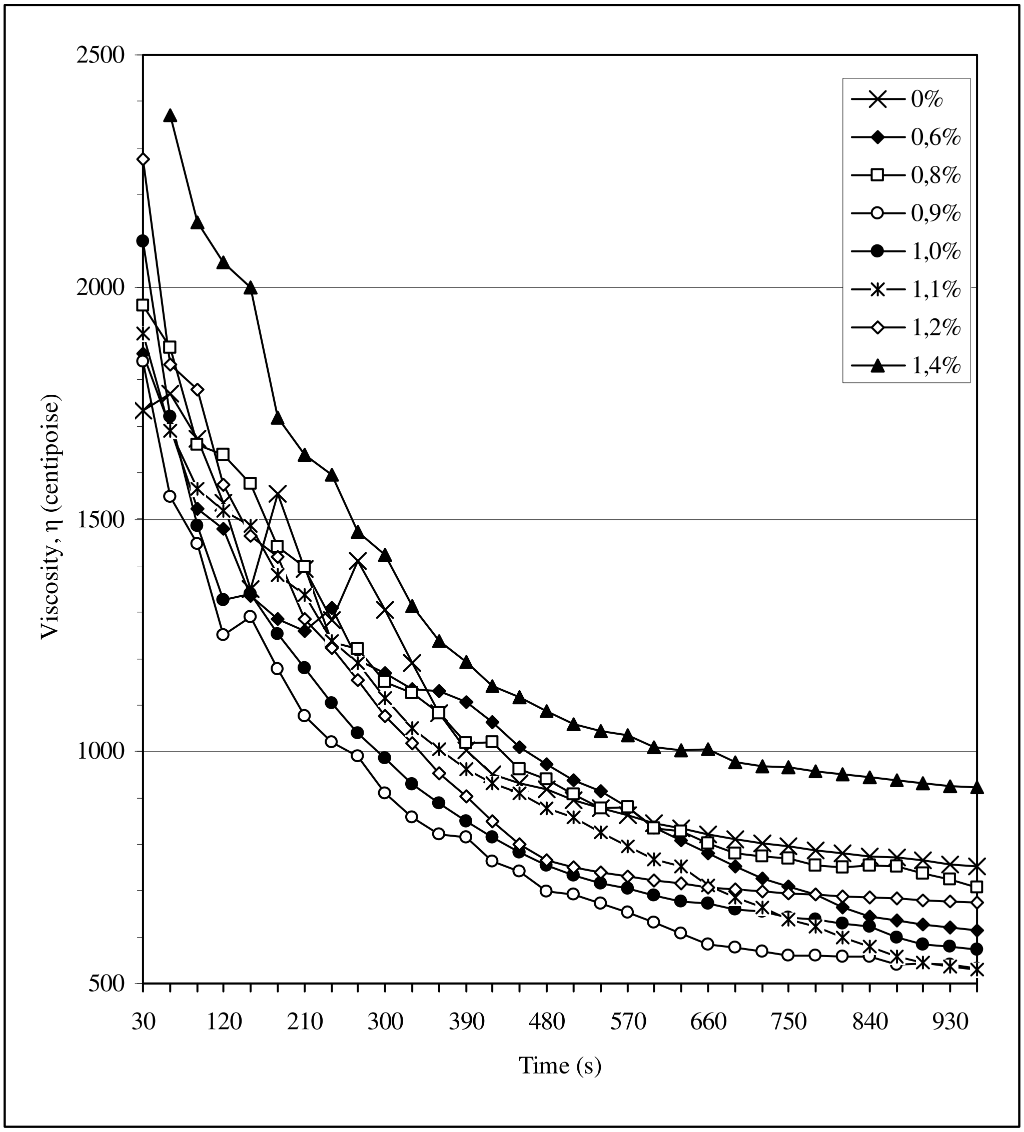

Figure 20. Effect of Chemical Agents Amount on Viscosity of CWMs

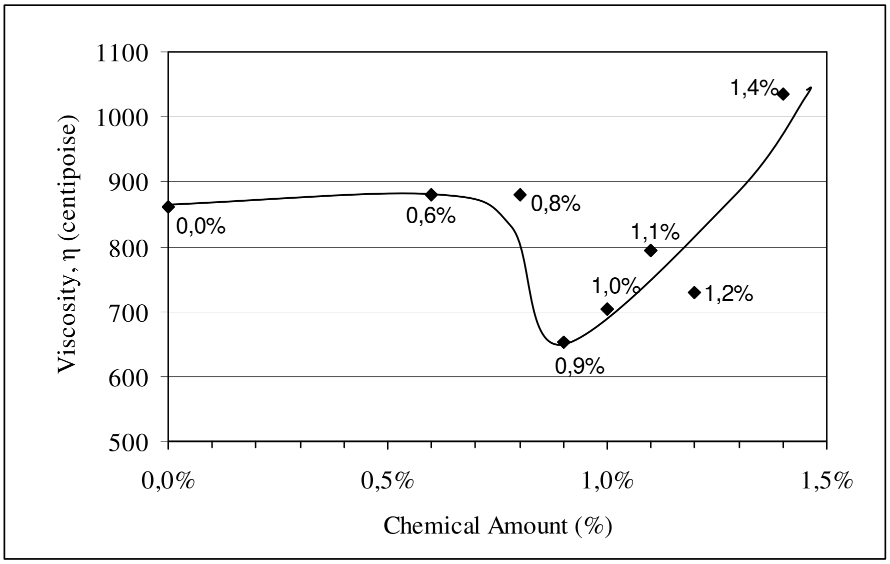

Figure 21. Change of viscosity as a function of amount of chemical agent in CWM at the 570th sec.

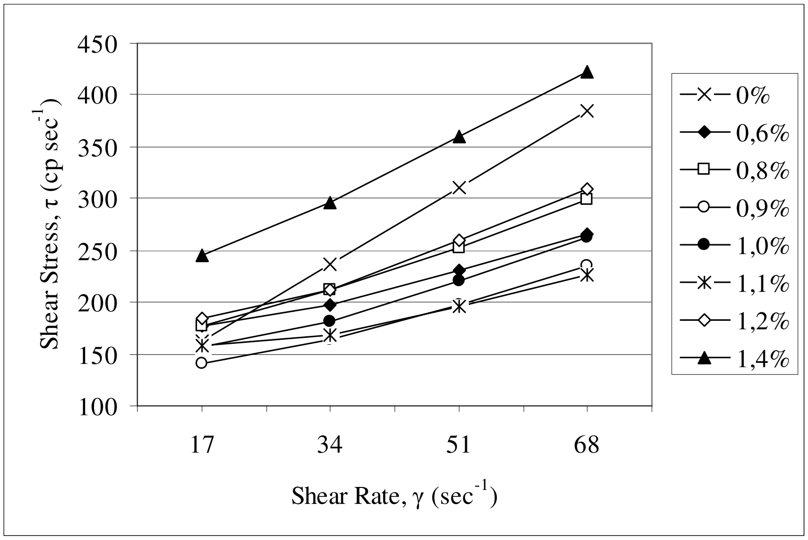

Figure 22. Shear Rate vs. Shear Stress for Different Ratios of Chemical Agents

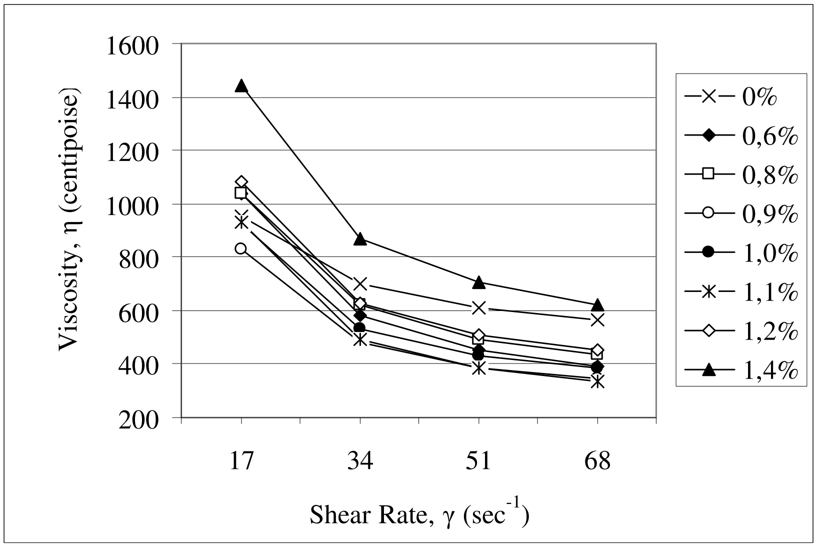

Figure 23. Shear Rate vs. Viscosity for Different Ratios of Chemical Agents

From the Figures 20, 21, 22 and 23 it is seen that the experiments in which 0.9 %, 1.0% and 1.1 % chemical agent used have results close to each other. The viscosity and the shear stress are having minimum value when the total chemical agent amount was 0.9%. Therefore, the following experiments were continued by using 0.9% chemical agent by weight. Hiçyılmaz et al. (2006) obtained the lowest viscosity value for Asphaltite-Water Slurries at 1.1% by using the same chemical agents having same ratio.

From Figures 20 and 21, it can be seen that the mixture which has no chemical in it, has higher viscosity than the mixtures having chemical agent except 1.4%. Also, there is a fluctuation in the viscosity values due to instability of pulp which shows the importance of Na-CMC. The reason of high viscosity of mixtures having 1.4% chemical is probably due to the high content of Na-CMC.

Na-CMC is a strong polymer agent and presence of excess Na-CMC concentration would cause a bridging mechanism between coal particles, leading to the formation of a network of aggregates or flocculates. This would have obviously resulted in an increase in the viscosity of CWMs.

To investigate the necessity of chemical agents, CWM with 0.9% chemical agent (60% pulp density) was stored in beaker for 5 days and the experiment was repeated after 5 minutes mixing. As seen in the Figure 24, the viscosity of mixture still has same rheological behaviour but the viscosity increased slightly. This result shows the importance of chemical agents. The same experiment was done for CWM without any chemical agent (Figure 25) and the results were compared in Figure 26. Without Na-CMC and PSS, mixture is not stable and well dispersed.

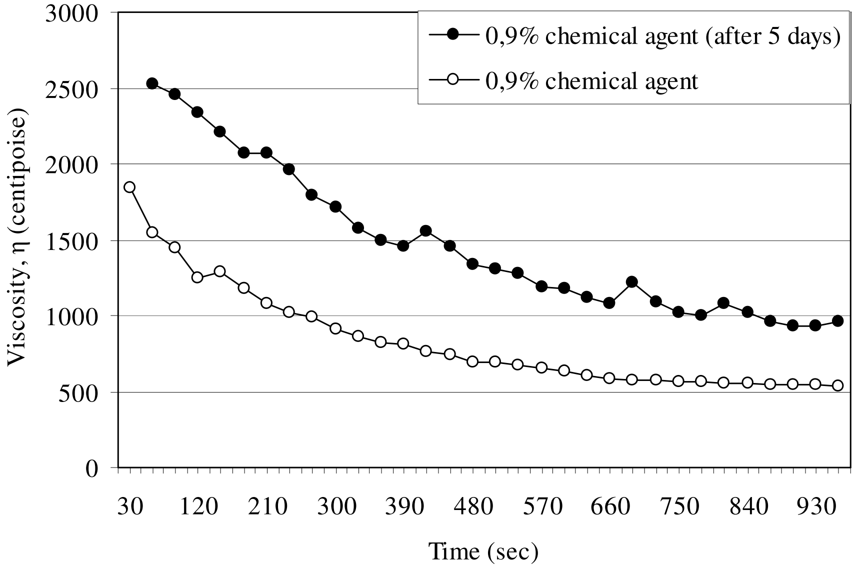

Figure 24. The change in viscosity when the experiment was repeated after 5 days (0.9% chemical agent and 60% pulp density)

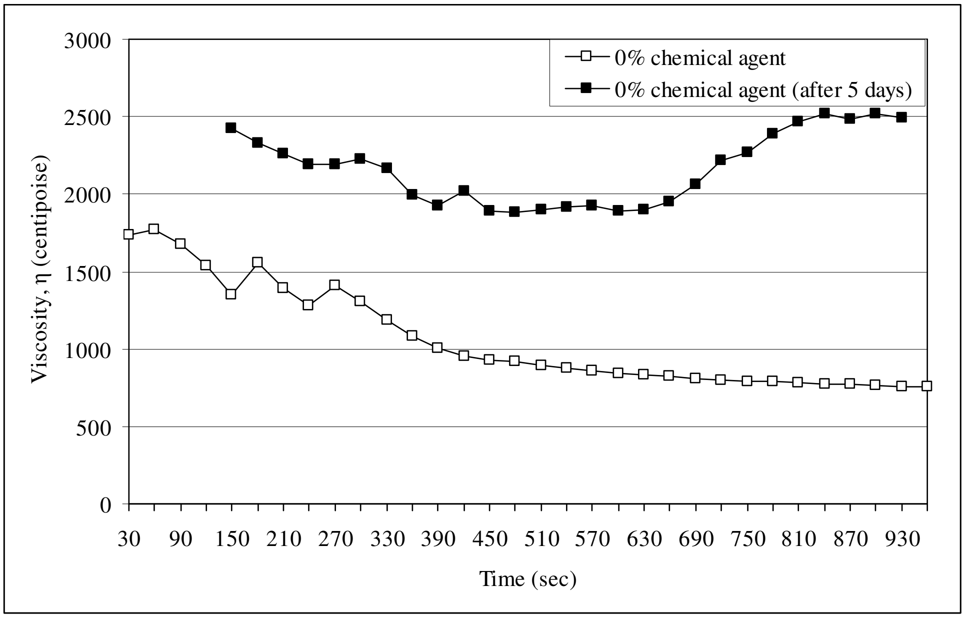

Figure 25. The change in viscosity of CWM without any chemical agent, when the experiment was repeated after 5 days (60% pulp density)

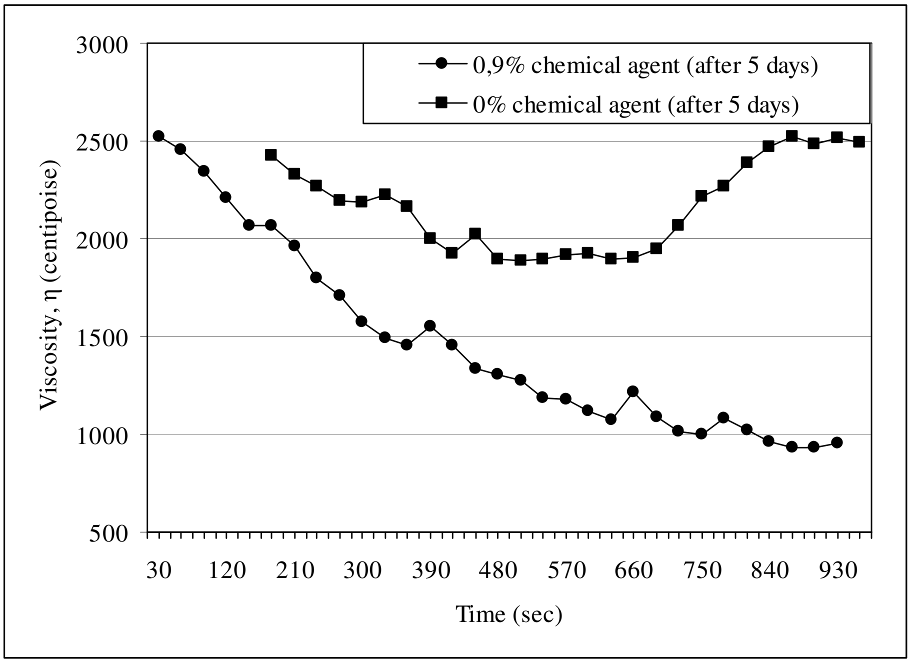

Figure 26. The comparison of CWM with 0.9% chemical agent and CWM without any chemical agent after 5 days (60% pulp density).

The results given in Figures 24, 25 and 26 show that chemical agents, namely PSS and Na-CMC, are necessary for low viscosity and good stability. The CWMs without chemical agent showed higher viscosity and poor stability which resulted fluctuation in viscosity as it can be observed in Figure 25. Moreover the viscosity value differences between the experiments done immediately and after 5 days were higher when the CWMs have not chemical agent. The viscosity values of CWMs having 0.9% chemical agent were much closer to each other. Also, as it is seen from Figure 26, they have different flow behaviours. The mixture with 0.9% chemical agent showed thixotrophic behaviour during the measurement (16 minutes) however, the mixture without any chemical agent exhibited rheopectic behaviour after 600^{th} second of measurement. On the other hand, the higher viscosity values of 5 day waiting experiments were probably due to the evaporation of water in slurry and inclusion of water into the fine crack and pores of coal which result the lowering of free water within the CWMs.

6.2.1 Effect of CMC/PSS Ratio

Dispersion and stabilization of the pulp were the main requirements for pumping and pulverization of CWM to a combustion chamber. Amount of chemical agents added into pulp is critical to get good dispersing stability and low viscosity as mentioned and discussed previously.

In this set of experiments, the amount of total chemical agent was kept constant (0.9%); and the ratio of PSS/CMC was changed to observe the effect of it and to find an optimum ratio. The results are given in figures 27, 28, 29 and 30.

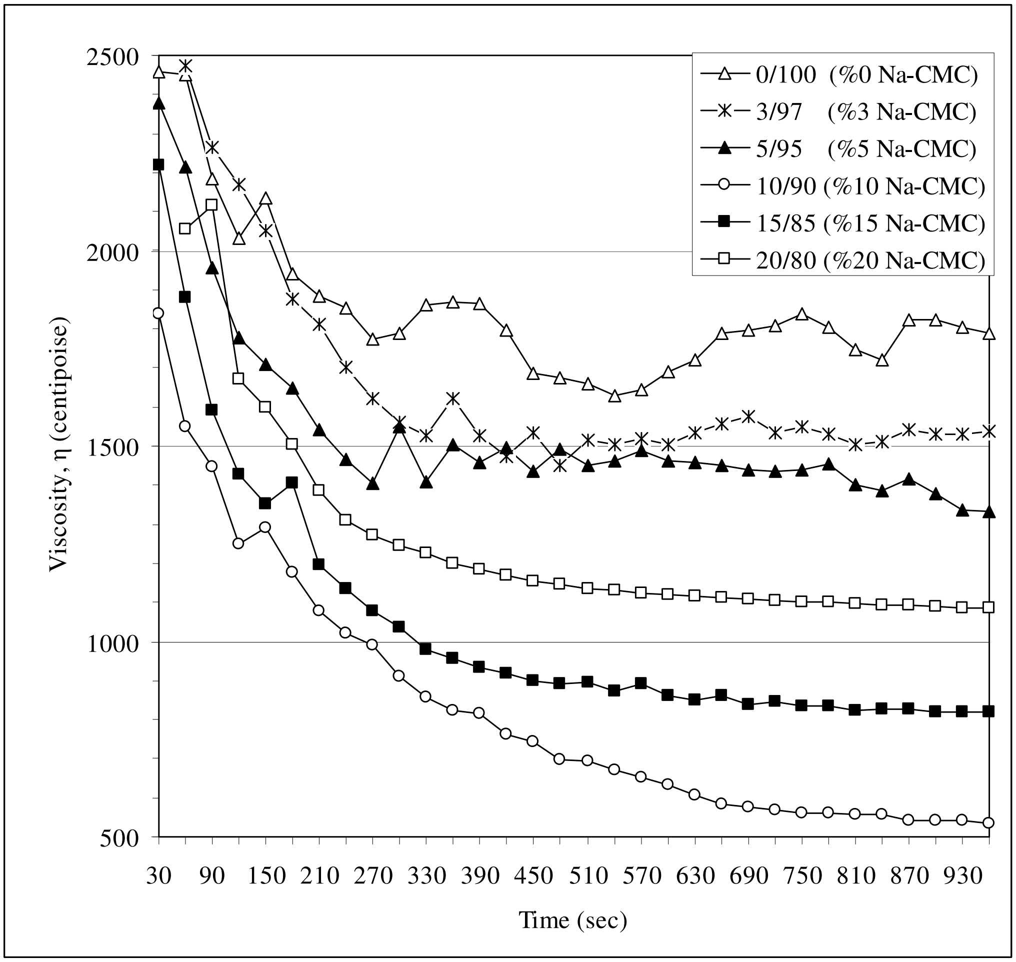

Figure 27. Effect of CMC/ PSS ratio on Viscosity of CWM.

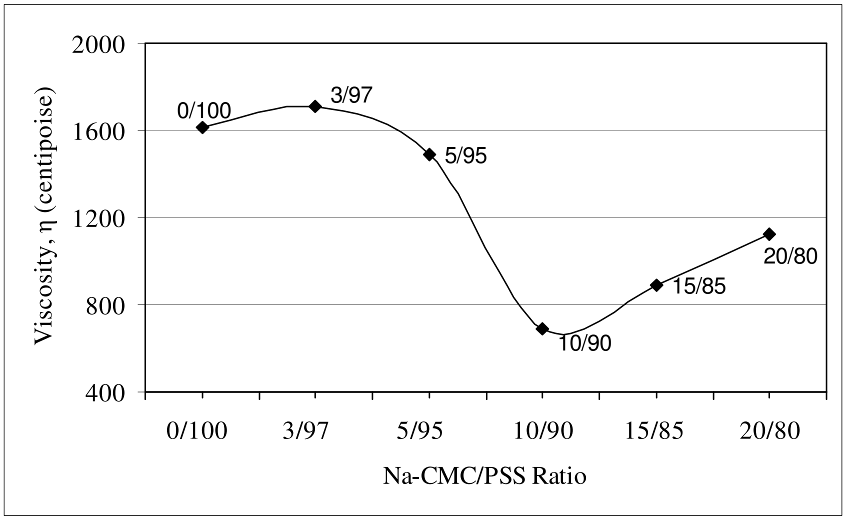

Figure 28. Change of viscosity as a function of the CMC/PSS ratio

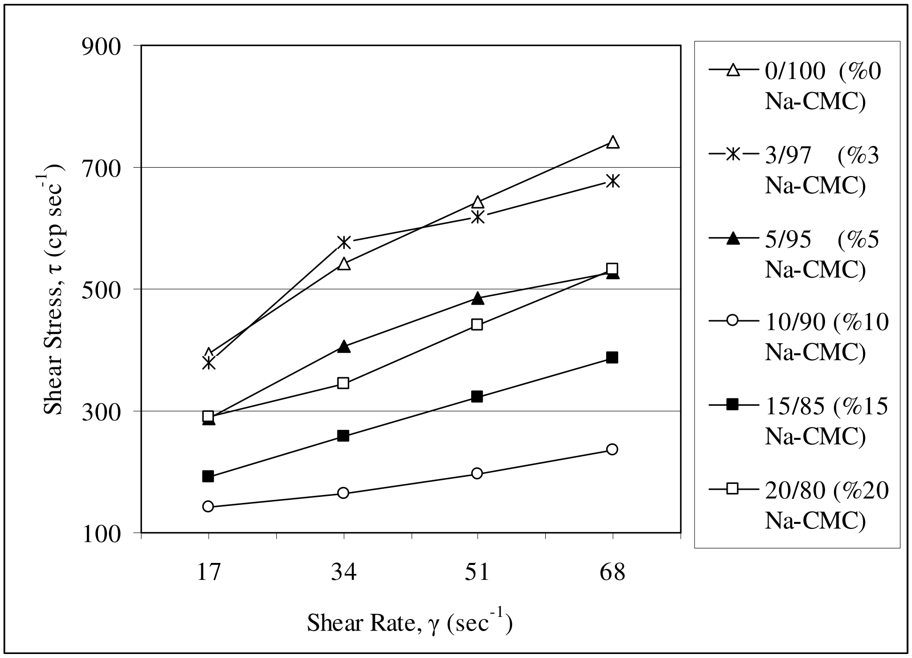

Figure 29. Shear Rate vs. Shear Stress for Different CMC/PSS ratios

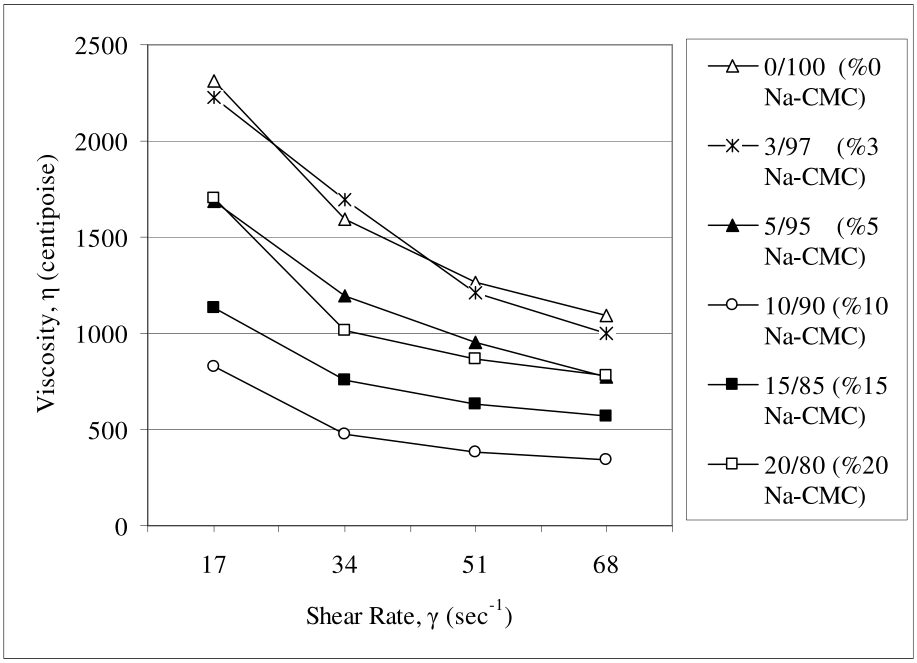

Figure 30. Shear Rate vs. Viscosity for Different CMC/PSS ratios

The results show that the mixture which contains 10% CMC and 90% PSS has minimum viscosity and shear stress. The mixtures containing 15% and 20% CMC display higher viscosity and shear stress than 10% CMC content mixture. The changing of apparent viscosity is regular and decrease gradually with time in all 10%, 15% and 20% CMC containing mixtures. The viscosity of mixtures having 5%, 3% and 0% Na-CMC decreased with time, however the viscosities were higher and fluctuate. As it is discussed before, Na-CMC is a polymer agent and excess amount of it cause a bridge between coal particles and form aggregates or flocs which obviously resulted in an increase in the viscosity of CWMs. Therefore, 10% CMC were used in the following experiments.

6.3 Effect of Pulp pH on CWM

The effect of pulp pH on viscosity was studied with the lowest viscosity obtained with 0.9% chemical addition and 60% pulp density. pH was adjusted either by HCl or by NaOH. Table 5 shows the changing in pH values during the experiments.

Table 5. Changing in pH values during the experiments

	Liquid	(water+ coal+ PSS+ Na-CMC) **Mixed pulp**	**At the end of viscosity measurement**
NaOH			
	12.71	8.09	8.09
	12.62	7.48	7.44
	12.46	7.24	7.26
	12.31	7.10	7.08
	12.15	7.02	7.02
	11.92	6.91	6.97
Natural			
	5.84	6.85	6.83
HCl			
	2.4	6.82	6.82
	2.05	6.79	6.79
	1.55	6.68	6.61
	1.24	6.55	6.52
	1.03	6.38	6.35

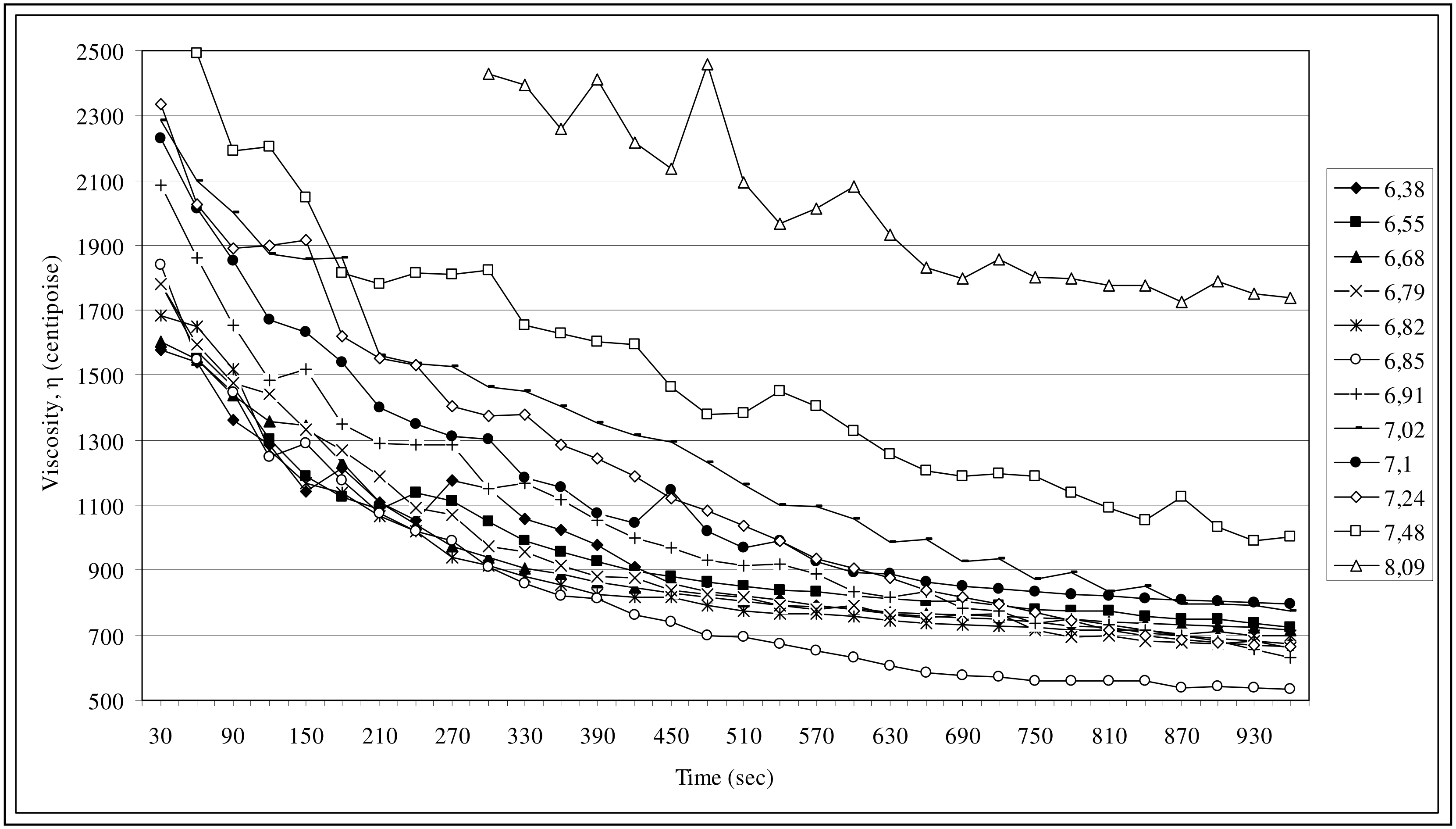

Figure 31. Effect of Pulp pH on Viscosity

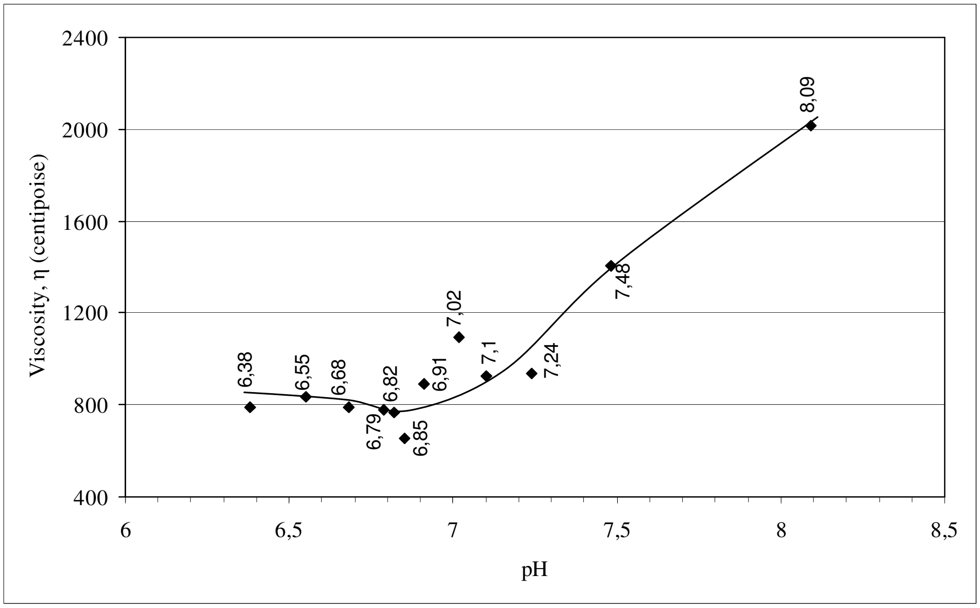

Figure 32. Effect of pulp pH on viscosity of CWM at 570th sec.

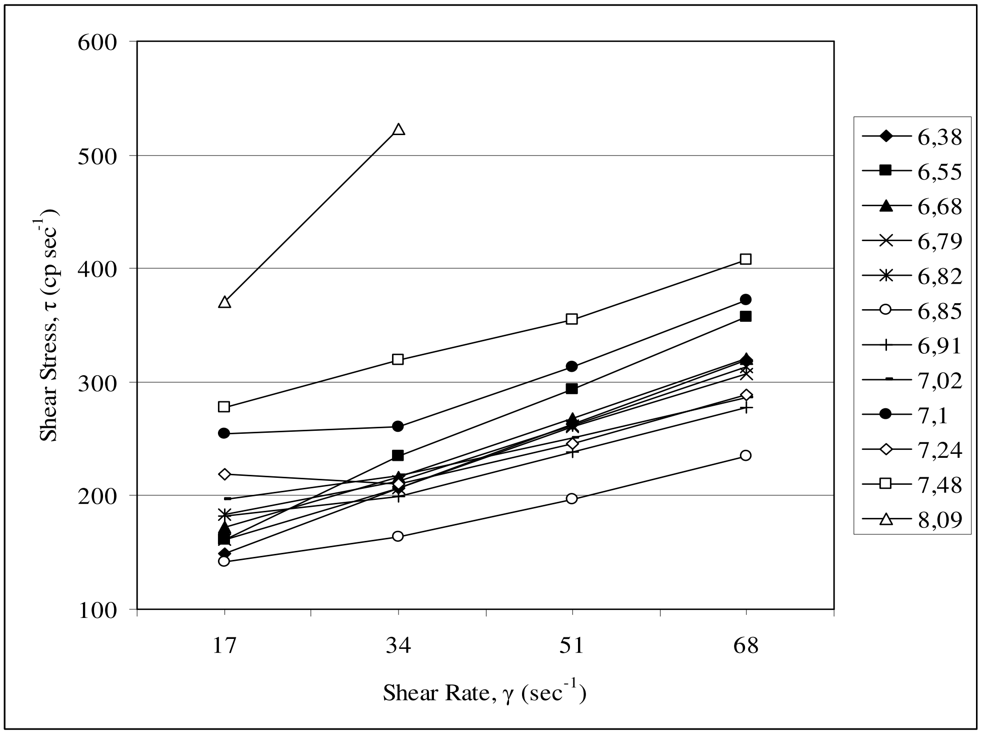

Figure 33. Shear Rate vs. Shear Stress for Different pH Values

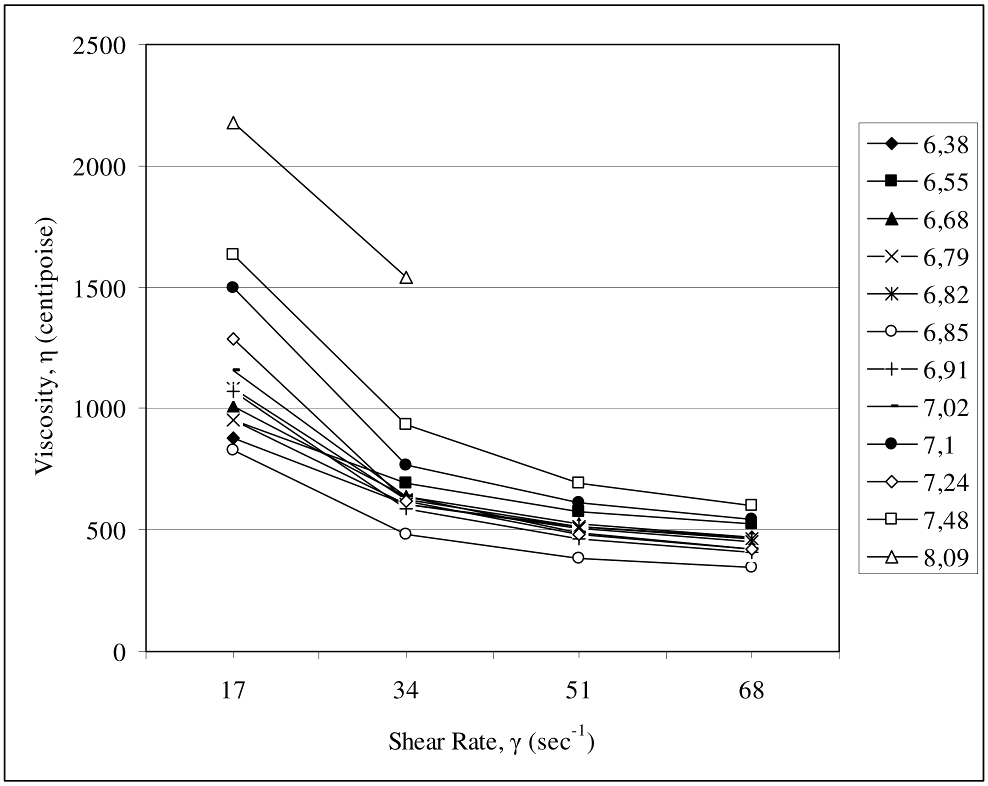

Figure 34. Shear Rate vs. Viscosity for Different pH Values

The effect of pH on the rheological properties of CWMs was studied with 0.9% chemical agent having 90% PSS and 10% Na-CMC as the lowest viscosity value was obtained. The results are seen in Figures 31, 32, 33 and 34. At all pH values, CWMs had non-Newtonian flow behaviour.

When the viscosity vs. time profiles of CWMs were evaluated as a function of pH, it was seen that the "thioxotropic" character was preserved at all pH values. The lowest viscosity value was obtained at natural pH of 6.85. The viscosity values increased as the pulp pH increase (i.e. at alkaline pH).

Figures 35 shows the zeta potential of coal particles vs. pH. The increasing of pH increased the zeta potential from -18 mV up to -40 mV which means that increase of surface charge. This tendency caused the expectation of lowering of viscosity with increasing of pH. However, as it is seen from Table 5, the adjusted highly acidic or alkaline pH values changed to closely natural values after the addition of PSS, Na-CMC and coal. Therefore the effect of pH values on viscosity of CWMs could not be exactly seen. This may be also due to the presence of carbonaceous mineral maters in the coal which caused the neutralization of pulp pH. The addition of higher amount of acid to reduce the pH was avoided not to change the mineral content of coal.

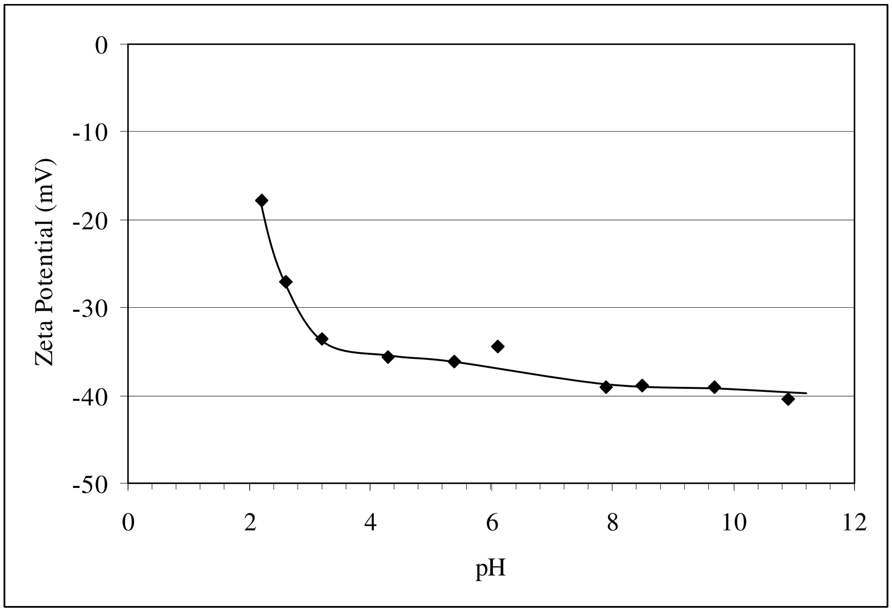

Figure 35. Zeta Potential of Coal Particles vs. pH

6.4 Effect of Particle Size Distribution

Coal samples were ground for 5, 10 and 15 minutes (d_{50}= 47.42µm, 33µm and 22.82µm) to see the effect of various particle size distributions on viscosity. Pulp density was 60% and amount of chemical agent was %0.9 in the experiments. The particle size distributions and their d_{50}, d_{80} and arithmetic mean values for 5, 10 and 15 minute of grinding were given in Figure 10 and Table 4, respectively.

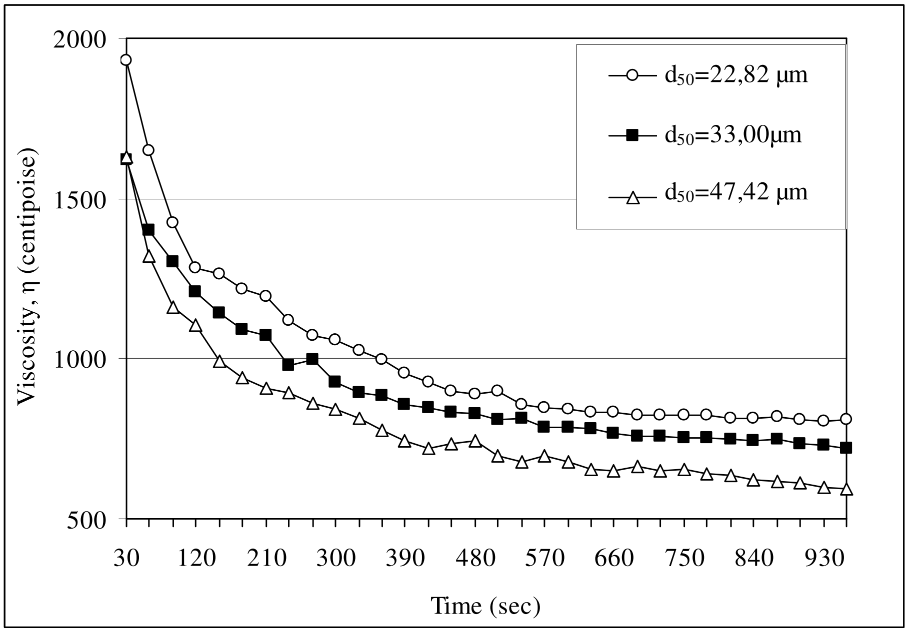

Figure 36. Effect of Particle Size Distribution on Viscosity of CWM.

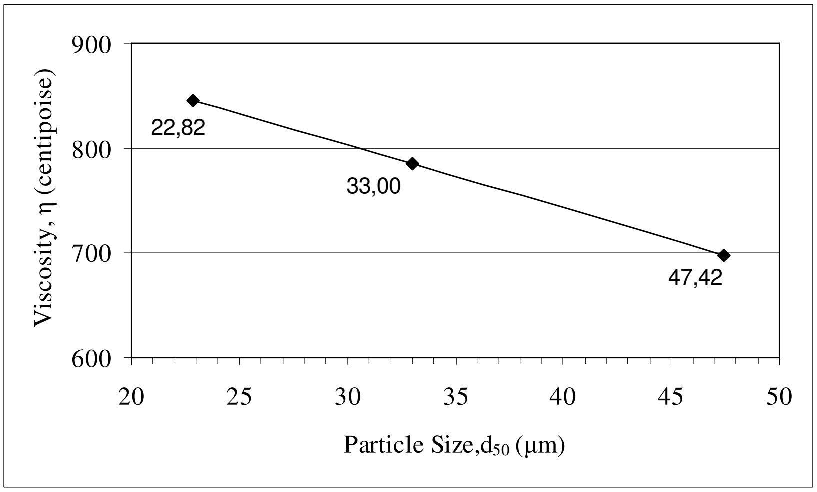

Figure 37. Change of Viscosity as a Function of Particle Size Distribution at the 570th sec.

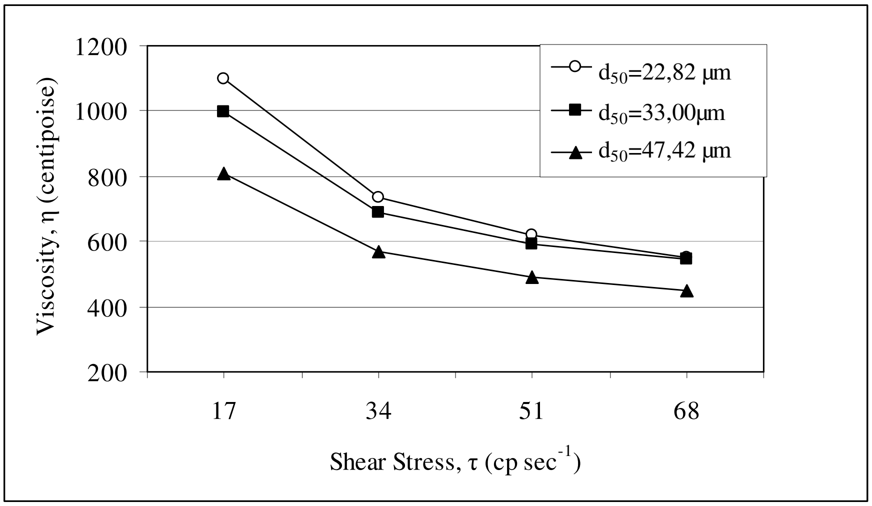

Figure 38. Shear Rate vs. Viscosity for Different Particle Sizes of CWMs.

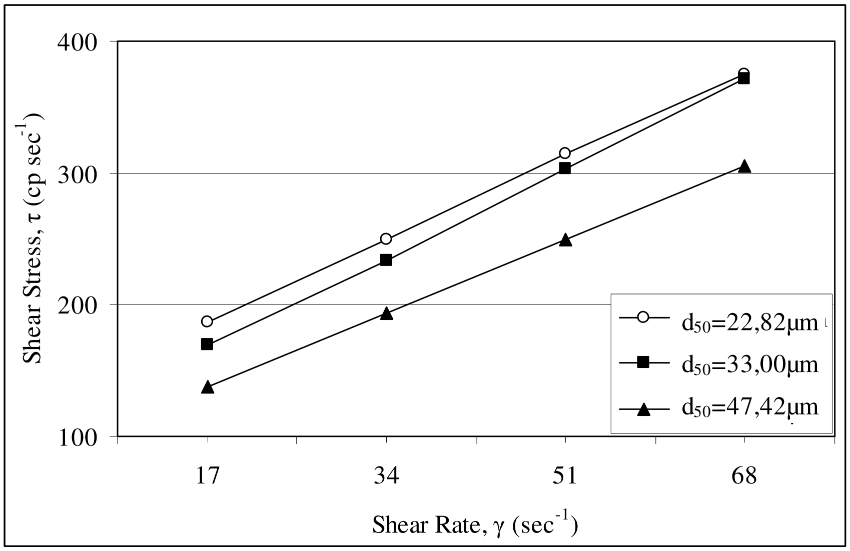

Figure 39. Shear Rate vs. Shear Stress for Different Particle Sizes of CWMs.

As it seen from the Figures 36, 37, 38 and 39, all CWMs exhibited non-Newtonian behaviour. The viscosity vs. time profiles tended to shift into a "thixotrophic" character. The coarsest particle size distribution, obtained after 5 minutes of grinding

(d_{50} = 47.42µm), showed the lowest viscosity values. Contrary, higher viscosity values over the entire range of measurement were recorded as the particle size became finer. The increase in the viscosity of CWMs with decreasing particle size is in conformity with previous results obtained by Ateşok et al. (2002), Boylu et al. (2003), and Hiçyılmaz et al. (2006).

The increase in the viscosity with a decrease in the particle size is related to the volume fraction aspect. The volume fraction is defined as the ratio of the volume of a known amount of particles after vibrating in a graduated cylinder for a certain period of time to the initial bulk volume. The volume fraction is simply found according to the following equation:

$$V_R = V_F / V_I$$

where; V_R is the volumetric ratio,
V_F is the volume after vibrating in the graduated cylinder (in cm^3),
V_I is the bulk volume (in cm^3).

When the particle size distribution is finer, volumetric ratio becomes lower. This is because a more compact network is achieved as the ultra fine and fine particles are easily located within the voids between relatively coarse particles. The liability of the individual particles to agglomerate increases as a result of this compact structure and reduced distance between the particles, i.e., increased extent of interparticular attraction. Also, as the fine particles fill the voids, the amount of free space available for the penetration and free flow of water abruptly decreases. This reduces the lubricating effect of water during the bypass of particles along with each other and increases the interparticular friction, and thus, the viscosity of CWM. In case of a wide range of particle size distribution, fine particles fill the gaps between coarse particles and therefore higher volume fractions can be obtained (Boylu et al., 2003). Keller and Keller (1991) suggested that when the particle size range increased, the viscosity values dropped at low shear rates because of the decrease in Brownian movements. However, it is a necessity to grind coal to very fine sizes for the preparation of CWM to prevent possible sedimentation during pumping and storage and to provide appropriate atomization and combustion of fuel-water slurries in the boilers. Allen (1984) determined that because of the burning process limitations, the maximum particle size should not exceed 250 μm and it was also indicated that generally 70-80% of particles should have a diameter less than 75 μm with a mean particle diameter between 20 and 30 μm (McHale, 1985).

6.5. Effect of Using Methyl Alcohol in CWMs

In these experiments, methyl alcohol is added to coal-water mixture which has 0.9% chemical agent (PSS and Na-CMC). The amount of methyl alcohol used was 2%, 5%, 10% and 20% of water in the mixtures. The results were given in Figures 40, 41, 42 and 43. The aim of using methyl alcohol in CWMs was to investigate the possibility of decreasing of viscosity which has an advantage of increasing the combustibility of CWMs in power plants. However as it is seen from Figure 40, 41, 42 and 43, methyl alcohol not only increased the viscosity but also damaged the stability of CWMs. This result was obtained probably negative effect of methyl alcohol on PSS and Na-CMC. Özdemir (1997) used ethanol as a polar solvent and found that adding ethanol increases the viscosity of CWMs and determined that this result may be because of the hydrophilic character of ethanol.

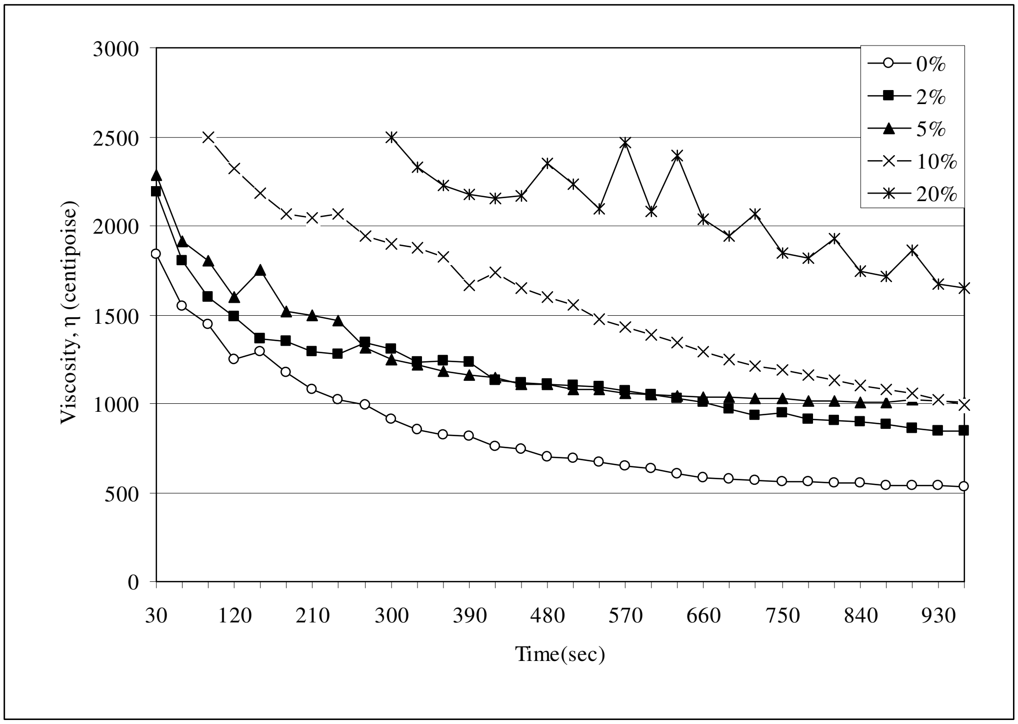

Figure 40. Effect of Methyl Alcohol on Viscosity of CWMs (60% pulp density, 0.9% chemical agent).

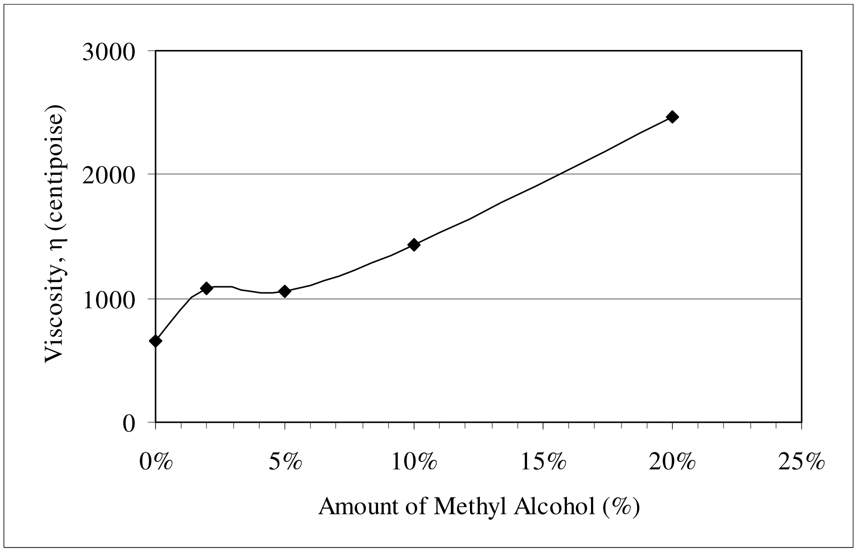

Figure 41. Change of Viscosity as a Function of Addition of Methyl Alcohol at 570th sec. (liquid% by ml)

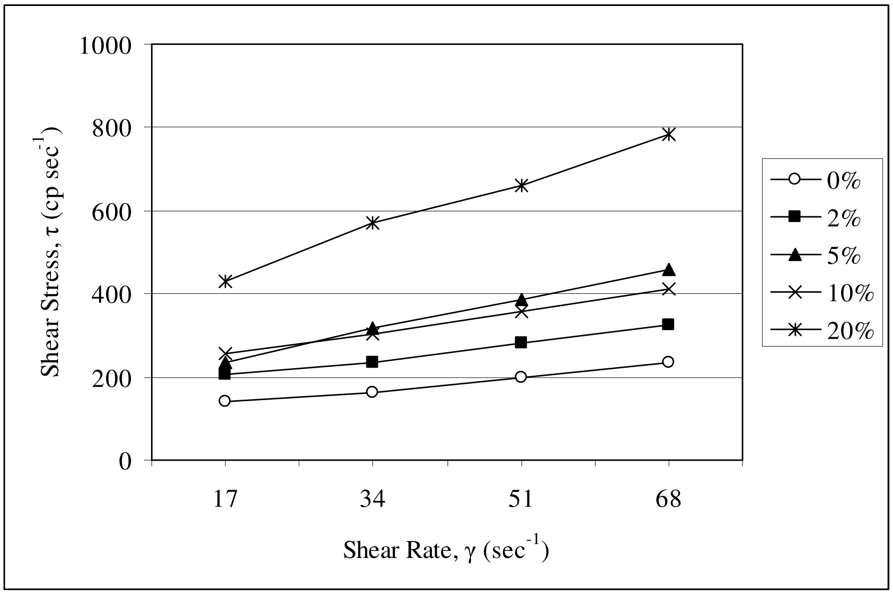

Figure 42. Shear Rate vs. Shear Stress as a Function of Methyl Alcohol

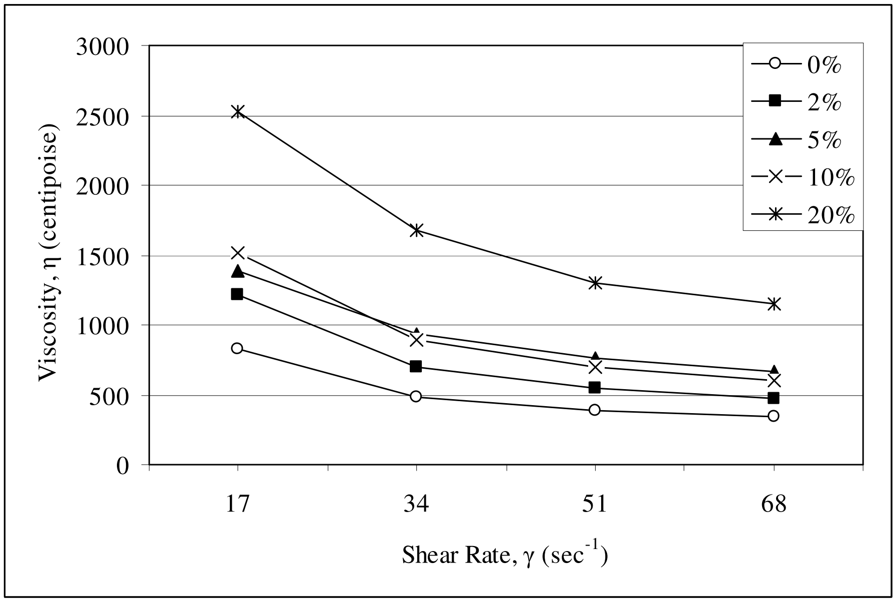

Figure 43. Shear Rate vs. Viscosity as a Function of Methyl Alcohol

CHAPTER 7

CONCLUSION

In the investigation, the effect of pulp density, chemical agent amount, pulp pH, methyl alcohol and particle size distribution on viscosity of coal-water mixtures were studied with Çayırhan lignite. The results showed that all these parameters are very important to obtain stable and homogeneous CWM with low viscosity.

In all experiments, CWMs of Çayırhan lignite showed non-Newtonian thixotrophic and shear-thinning behaviour which means that viscosity of mixtures decreases with time and shear rate.

The critical pulp density was found as nearly 62% solid by weight. At this pulp density, viscosity increased sharply. 60% pulp density was found as the optimum value when d_{50}=22.82 µm. Increasing pulp density, negatively affect viscosity because interparticular friction and resistance to flow increased.

The CWM with 0.9% chemical agent showed the lowest viscosity. At the amounts of lower or higher than this value, higher viscosities were obtained. Also, CMC/PSS ratio was studied while the total amount of chemicals kept constant as 0.9%. When the CMC/PSS ratio was 1/9, the lowest viscosity value was obtained. These results showed that, dosages of chemicals are very critical to get good dispersing stability and low viscosity; the excess use results an increase in viscosity.

Although pulp pH is another important parameter that affects viscosity of CWM, it could not be seen. The lowest viscosity value was obtained when the pulp pH was natural (6.85); without adding any acid or base. The viscosity negatively affected in both alkaline and acidic conditions. However, the increasing in viscosity was explicit in alkaline conditions.

The effect of particle size distribution is considerable. When the particle size increases, viscosity decreases. However, fine particle size distribution is necessary to get stable and homogeneous CWMs with low viscosity.

Finally, the addition of methyl alcohol to CWMs caused the increasing of viscosity of CWM.

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APPENDIX

Table A.1. The amount of coal, water and chemicals used in different pulp densities

Pulp density (solid% by weight)	Amount of Coal (g)	Amount of Water (ml)	PSS (ml)	Na-CMC (2.5% solution) (ml)
54%	70	56.20	0.63	2.80
56%	74	54.51	0.67	2.96
58%	77	52.00	0.70	3.08
60%	80	49.41	0.72	3.20
62%	85	47.93	0.77	3.4

Table A.2. Variation of coal, water, PSS and Na-CMC with the increasing of chemical amounts

Chemical Agent (% by weight)	Amount of Coal (g)	Amount of Water (ml)	PSS (ml)	Na-CMC (2.5% solution) (ml)
0%	80	53.34	0	0
0.6%	80	50.98	0.43	1.92
0.8%	80	50.20	0.58	2.56
0.9%	80	49.81	0.65	2.88
1.0%	80	49.41	0.72	3.20
1.1%	80	49.03	0.79	3.51
1.2%	80	48.63	0.86	3.84
1.4%	80	47.85	1.01	4.48

Table A.3. The amount of coal, water, PSS and Na-CMC with the variation of Na-CMC/PSS ratio

Na-CMC/PSS	Amount of Coal (g)	Amount of Water (ml)	PSS (ml)	Na-CMC (2.5% solution) (ml)
0/100	80	52.62	0.72	-
3/97	80	51.78	0.70	0.86
5/95	80	51.21	0.69	1.44
10/90	80	49.81	0.65	2.88
15/85	80	48.41	0.61	4.32
20/80	80	47.58	0.58	5.76

Table A.4. The amount of coal, water and chemical agents used for different pulp pH.

Pulp pH	Amount of Coal (g)	Amount of Water (ml)	PSS (ml)	Na-CMC (2.5% solution) (ml)	Amount of HCl or NaOH solution (ml)
6.38	80	39.81	0.65	2.88	10.0
6.55	80	43.81	0.65	2.88	6.0
6.68	80	46.81	0.65	2.88	3.0
6.79	80	48.81	0.65	2.88	1.0
6.82	80	49.31	0.65	2.88	0.5
6.85	80	49.81	0.65	2.88	0
6.91	80	49.31	0.65	2.88	0.5
7.02	80	48.81	0.65	2.88	1.0
7.10	80	48.31	0.65	2.88	1.5
7.24	80	47.81	0.65	2.88	2.0
7.48	80	46.81	0.65	2.88	3.0
8.09	80	44.81	0.65	2.88	5.0

Table A.5. The amount of coal, water and chemical agents used for different particle size distributions.

Particle Size Distribution	Amount of Coal (g)	Amount of Water (ml)	PSS (ml)	Na-CMC (2.5% solution) (ml)
d_{50}= 22.82 μm	80	49.81	0.65	2.88
d_{50}= 33.00 μm	80	49.81	0.65	2.88
d_{50}= 47.42 μm	80	49.81	0.65	2.88

Table A.6. Variation of coal, water and chemical agents with the increasing of methyl alcohol

Amount of Methanol (%)	Amount of Coal (g)	Amount of Water (ml)	PSS (ml)	Na-CMC (2.5% solution) (ml)	Amount of Methanol (ml)
0%	80	49.81	0.65	2.88	0
2%	80	49.71	0.65	2.88	0.1
5%	80	47.32	0.65	2.88	2.49
10%	80	44.83	0.65	2.88	4.98
20%	80	39.85	0.65	2.88	7.97