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EFFECT OF BLACK LIQUOR FROM DATE PALM ON THE WORKABILITY AND COMPRESSIVE STRENGTH OF PORTLAND CEMENT AND CONCRETE

ABSTRACT

Abstract - Lignin is the second most abundant natural polymer. Due to the high content of carbon and hydrogen (C-H, C-C, C=O), it can be used as a potential dispersant for cement matrix. The objective of this study is to extract lignin from date palm and study its effect in the form of black liquor (BL) on the rheological and physic-mechanical properties of the cements and concrete. The lignin in black liquor form represents approximately 30 wt% dry weight of date palm. It is a heteropolymer composed primarily of methoxylated phenylpropylene alcohol monomeric units interconnected by a variety of stable carbon-carbon and carbon-oxygen-carbon (ether and esters) linkages. The results found show the positive effect on the workability of cement and concrete and confirms its dispersion effect by improving compressive strength of concrete during the early and the later ages of hydration.

Keywords: *black liquor (BL), date palm, cement, rheological properties, compressive strength*

INTRODUCTION

Interest in renewable feedstock for the chemical industry has increased considerably over the last decades, mainly due to environmental concerns and foreseeable shortage of fossil raw materials. Lignocellulosic biomass is an abundant source of bio-based raw material that is readily available and can be utilized as an alternative source for chemical production [1-4].

Lignin is one of the important chemical constituents of lignocellulosic materials in wood and it is one of the most abundant biopolymers in nature. Despite extensive investigation, the complex and irregular structure of lignin is not fully understood. The physical property and the chemical characteristics of lignin vary not only between different wood species, but also according to the method of isolation. Moreover, the molecular structure and function groups differ for the various type of lignin [4- 9].

Lignin, a heterogeneous three-dimensional biopolymer, is one of the building blocks of lignocellulosic biomass. It is a complex biopolymer, which contains a large number of functional groups, including aliphatic and aromatic hydroxyl groups, carbohylic groups and methoxy groups in its structure that is why it shows potential capacities for process of sorption [10-11]. Lignin is a highly cross-linked polymer with a three-dimentional structure which can provide large surface area and pores volumes [8, 12, 13].

Based on the source (softwood, hardwood or annual crop) and isolation method (Kraft, organosolv, sulfite or preenzymatic treatment), there are significant variations in lignin structure and properties. The first step in using lignin as biobased feedstock is to make sure that specific lignin is suitable for intended application. Complete characterization of lignin and measuring its chemical, physical and thermal properties can help to predict its suitability [14, 15].

In this study, we extracted the lignin by the Kraft process from the date-palm wood of the TOLGA-Algeria region. After extraction and sulfonation the Kraft lignin has been valued as superplasticizer in concrete. Its physical characteristics and its rheological effect to the cement matrix have been studied.

MATERIALS AND METHODS

Kraft Lignin

Lignin is a complex chemical compound and the only aromatic polymer present in wood; it is concentrated mainly in the region of the middle lamella. The amount of lignin in normal wood is 20%-35% depending on the different wood species [16].

Lignin is an aromatic heteropolymer composed of three main monomers: p-hydroxyphenol (H), guaiacyl (G), and syringyl (S)-with varying degrees of methylation (Fig. 1). It is the nature of lignin and its bonds to hemicellulose and cellulose that determine how difficult it will be to breakdown lignocelluloses [17, 18].

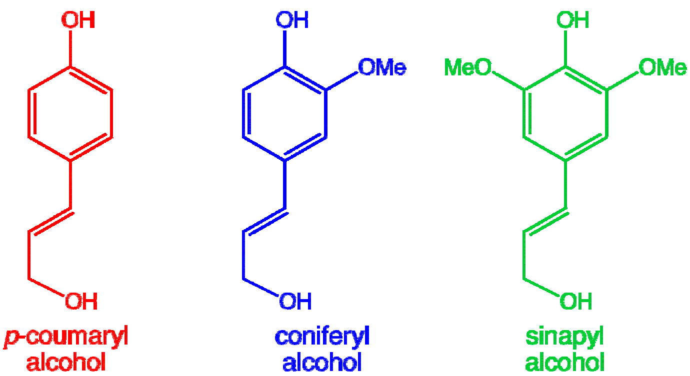

Fig. 1. Lignol Structures. Chemical structure of lignin alcohol precursors, the lignols, that incorporate into lignin as phenylpropanoids. The three main lignin phenylpropanoids are: p-hydroxypheyl (H), guaiacyl (G), and syringyl (S) [17, 18]

Isolation of lignin

The wood species sampled is the date palm. This species was chosen because of its great abundance in our country. Harvesting of this "date palm trunk" sampling was carried out in the Dkhila Tolga area of Biskra, Algeria.

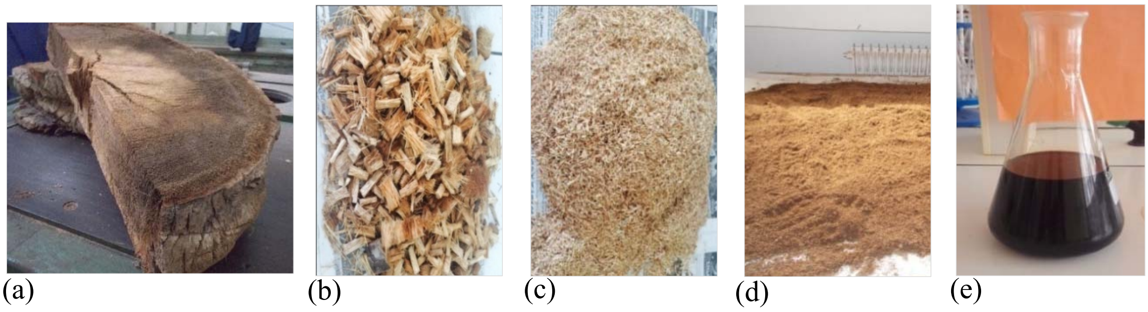

Fig. 2. Steps of processing of date palm wood: (a) Date palm trunk, (b), (c) The date-palm wood chips, (d) The milled wood, (e) The Black Liquor

Accordingly, the so-called dissolved wood lignin (DWL) method was developed by total dissolution of ball-milled wood. The date-palm wood chips, collected after shredding the tree trunk were dried (vacuum, 120°C, 48 h) and milled with a cutting mill to pass a 0.8 mm. The milled wood was extracted with toluene-ethanol/water (9:1) in a Soxhlet apparatus for 24h. The extractive free wood was dried (105°C) for several days [19]. The dry wood was milled with a planetary ball mill (Retsch PM2) with steel jars and steel balls under conditions specified below (Fig. 2).

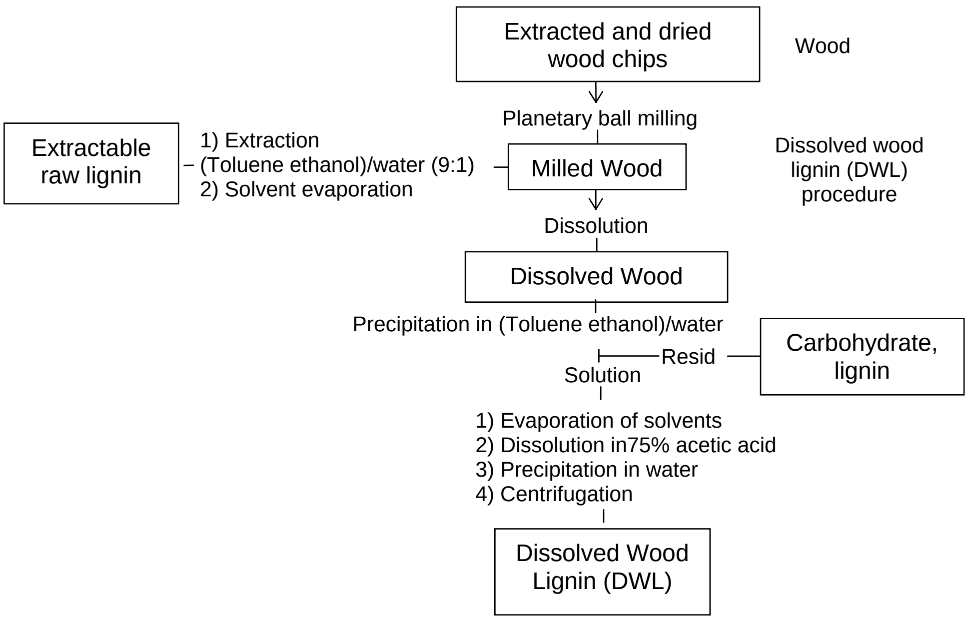

Fig. 3. Lignin isolation procedure (DWL) [19]

The solution collected was acidified to (pH 1.7), by using a dilute H_2SO_4 solution, and lignin was precipitated and separated by centrifugation. Upon completion, the wood meal dioxane mixture was filtered on a Buchner funnel and the residue was washed with a dioxane solution (9:1), after which it was neutralized by adding solid Na_2CO_3 and filtered. The filtrate was concentrated in a vacuum evaporator at 50 °C, and a concentrated dioxane solution was added dropwise, to precipitate the lignin. Finally, the precipitated lignin was washed with distilled water and dried (Fig.3).

Typical yields of lignin after a final extraction step were 31% on dry wood. Table 1 gives Properties of lignin in the form of Black Liquor.

***Table 1**. Properties of lignin (Black Liquor)*

Density	pH	Water solubility, (g/L)	Dry extract (%)
1.12	12.16	1,9	7,9

Black Liquor FT-IR Analyses

FT-IR analysis was used to characterize the absorption bands for representative functional groups in the lignin extracts. Table 2 lists the peaks observed, as well as their assignments using previously described biomass samples in the literature [20-25].

The FTIR spectrum of lignin is shown in Fig. 4. Bands were assigned according to Shen et al. (2010) [26], and Yuan et al. (2011) [27]. The bands around 3350-3400 cm^{-1} is due to strong O–H stretching. Peaks at 2953-3080 cm^{-1} indicate apparent C–H stretching in methyl and methylene groups.

***Table 2.** Absorption peak assignment in FT-IR spectra of Black Liquor*

Approximate Band (cm^{-1})	Assignment
3350–3400	O–H stretching in hydroxyl groups
2953-3080	C–H stretching in methyl and methylene groups, C–H stretching aromatic methoxyl groups
1633	Aromatic skeleton vibrations plus C=O stretching
1375	Aliphatic C–H stretching in methyl and phenol OH
1225	secondary alcohol and C=O stretch
875	C–H vibrations

Stretch at 1633cm^{-1} corresponds to the existence of C=O in unconjugated carbonyls. C–H deformations can be found at 1375 cm^{-1}. The C=O stretch assigned to syringyl rings is presented at 1225 cm^{-1} as well as the C–H vibrations found at 875cm^{-1}.

The Black Liquor peaks are typically easier to characterize, and have significant absorbance peaks that enable the clear conclusions derived from the FT-IR spectra and confirms the obtaining of lignin by the method Dissolved Wood Lignin (DWL).

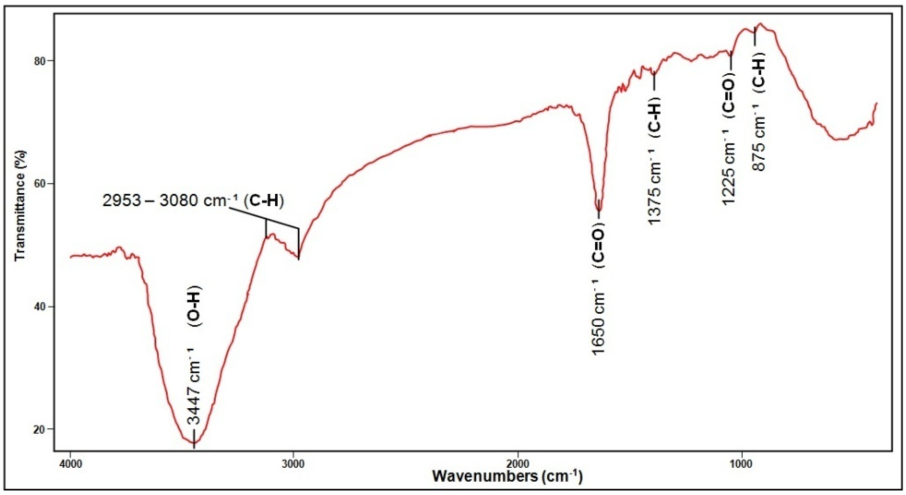

Fig. 4. Fourier transform infrared spectroscopy spectra of black liquor

Cement

The cement used in this study is a CPJ-CEM II/A 42.5 type, supplied by GICA Company, Algeria. It is characterized by a Normal consistency of 26.7% and a finesse following Blaine's method (NA 231) [28] of 5820 cm^2/g. The mineral and chemical compositions of cement are given in the Table 3 and 4, respectively.

Table 3. *The cement (CPJ-CEM II/A 42) mineral composition*

Mineral composition (%)	C3S	C2S	C3A	C4AF	Free CaO
CPJ-CEM II/A 42.5	53.90	21	7.11	11	≤ 1

Table 4. *The cement (CPJ-CEM II/A 42.5) chemical composition*

	Constituents		Per cent by Weight (%).
1.	Silica (SiO_2)		22.88
2.	Iron Oxide (Fe_2O_3)		5.42
3.	Alumina (Al_2O_3)		4.24
4.	Calcium Oxide (CaO)		62.93
5.	Magnesium Oxide (MgO)		1.03
6.	Total Sulphur (SO_3)		1.22
7.	Alkalies	a) Sodium Oxide (Na_2O)	0.24
8.		b) Potassium Oxide (K_2O)	0.37
9.	Insoluble residue		0.78
10.	Loss on ignition		0.89

Admixtures

A polycarboxylic ether based superplasticizer complying with NA 774 [29] type SIKAFLUID®-300, was used. Their properties are presented in Table 5.

Table 5. *Properties of superplasticizers SIKAFLUID®-300*

Properties	SIKAFLUID®-300.
Aspect	Dark brown
Specific gravity	1.195 ± 0.015
pH	7.5 ± 1.5
Chloride ion content	< 0.1 %
Maximum alkali content	< 4 %
Solid content	40 ± 1 %
Recommended dosage	0.5–3% by cement weight

Aggregates

Locally available natural sand with 5.12 mm maximum size was used as fine aggregate, having specific gravity, fineness modulus and unit weight and crushed stone with 20mm maximum size having specific gravity, fineness modulus and unit weight was used as coarse aggregate. Both fine aggregate and coarse aggregate conformed to Standard Specifications NA EN 933-1[30]. Table 6 gives the physical properties of the coarse and fine aggregates.

Table 6. *Physical Properties of Coarse and Fine Aggregates*

Physical tests	Coarse aggregate	Fine aggregate
Specific gravity	2.71	2.57
Fineness modulus	6.74	2.62
Bulk density (kg/m^3)	1556	1772
Absorption capacity (%)	0.43	1.17

RESULTS AND DISCUSSION

Tests on cement

Portland cement mortar was prepared at a water-cement ratio of W/C=0.35 and sand/cement ratio (S/C =3). Maximum amount of black liquor pulp added to the mix was limited to 2.5% because addition of higher amount of black liquor in concrete pulp leads to decrease in workability.

As the mixing sequence affect the properties of cement and concrete a uniform mixing sequence was adopted for preparing the mixes (Table 7). We set the W/C ratio to 0.35 and used five dosages of black liquor (0.5, 1, 1.5, 2 and 2.5%) by cement weight. Portland cement and aggregate were dry mixed first for two minutes and then water was added to the mix and mixed for 1 minute.

Table 7. *Mix proportion of cement past*

Mix designation	Cement (g)	Sand (g)	Water (g)	W/C	Black liquor dosages (g)
M0%BL	410	1240	143.5		0.0
M0.5%BL	410	1240	143.5		2.05
M1%BL	410	1240	143.5	0.35	4.10
M1.5BL	410	1240	143.5		6.15
M2%BL	410	1240	143.5		8.20
M2,5%BL	410	1240	143.5		10.25

M: Mortar, BL: Black Liquor

The properties of high performance concrete, mainly in the fresh state are governed by the flow behavior of the paste phase, which is controlled by the dispersion of cement particles by the superplasticizer [31]. In this study, experimental procedures for evaluating the flow behavior of mortar with different dosages of black liquor are studied. The rheological nature of the cement is represented through the Bingham and "Herschel-Bulkley" models [32].

Rheological tests on cement can be used to study the effect of the changes in cement, type and dosage of admixtures, such as superplasticizers, on paste characteristics like yield stress and plastic viscosity [33-37]. The principle is to apply different shear rates to the cement paste in a viscometer and measure the corresponding shear stresses. Generally, a loading-unloading cycle is applied to the cement paste, preceded by some pre-shearing, and the response during unloading is used to determine the rheological parameters [38-39]. Cement paste exhibits shear-thinning behavior, where the slope of the shear stress versus shear strain rate curve decreases with an increase in the shear rate. Such shear-thinning response is attributed to the structural breakdown and rebuilding that takes place in the cement paste [40], with the former mechanism predominating [41].

In the present study, a Brookfield HA DV II + Pro viscometer was used with a coaxial cylinder setup (Griffin Beaker of 600 ml in low form).

The shear stress-strain behaviour of mortar paste has been represented using several models [33], [42-44], the Herschel-Bulkley model, show Eq. (1) qualified more versatile model has been used by several researchers [32]:

$$\tau = \tau_0 + k\dot{\gamma}^n \tag{1}$$

Where τ is the shear stress in (Pa), $\dot{\gamma}$ is the shear strain rate (1/s), n is the power index, k is the consistency (Pas), and τ_0 is the yield stress (Pa).

Rheological behavior of cement pastes

The curves of shear stress and viscosity according to shear rate for different dosages of black liquor (0.5, 1, 1.5, 2 and 2.5% wt% cement), are shown in Figure 5.

The results show that fluidity increases with an increase in dosage of black liquor up to the saturation dosage, who equal to (2%) for M2% BL. We also notice that at a certain dosage the dough flows without any effort (absence of the yield value) is the saturation point (2%) for M2% BL, causing the decrease of the flow threshold (threshold constraint). The higher the percentage of black liquor increases the viscosity of the dough decreases until it is constant (almost Newtonian flow); this is due to the dispersing effect of the black liquor, which adsorbs at the cement grain interface, creating repulsive forces between the particles, reducing or eliminating the adhesion between adjacent particles [45].

Black liquor acts positively and specifically on the rheological properties of cement pastes. The intrinsic rheological parameters of the cement are determined by smoothing the experimental points of the rheograms. The smoothing model is that of Herschel-Bulkley (Equation 1).

Considering the case of the cement without the addition of the black liquor (BL), its rheogram and represented on the Figure 5. (a). Smoothing with the Hershel-Bulkley model leads us to the following rheological parameters; τ_0 = -0.07 Pa and a viscosity of μ = 6.209 Pa.s.

Substitution of water by black liquor gives rheograms to a rheo-thickening behavior and the viscosity of the mortar decreases. The best smoothing is recorded in the formulation (M2% BL) show Figure 5.(e). The parameters carried by the smoothing of the experimental points with the Hershek-Bulkly model are very good, the viscosity: μ = 0.01103 Pa.s and yield stress τ_0 = 2.494 Pa. This behavior is similar to that of self-compacting concretes with a fluidity index n> 1, which corresponds to rheo-thickening behavior which is generally reported in the literature [46].

Moreover, the addition of 2% BL with a W/C = 0.35 begets a better fluidity with the absence of segregation, the emulsifying aspect of the black liquor restrains the grains of cement, which separates the coarse grains by decreasing the friction between them.

The black liquor tested resulted in pastes with good fluidity, when the corresponding saturation dosages were used. It is concluded that the cement-black liquor combinations studied here are all compatible as far as the flow behavior is concerned.

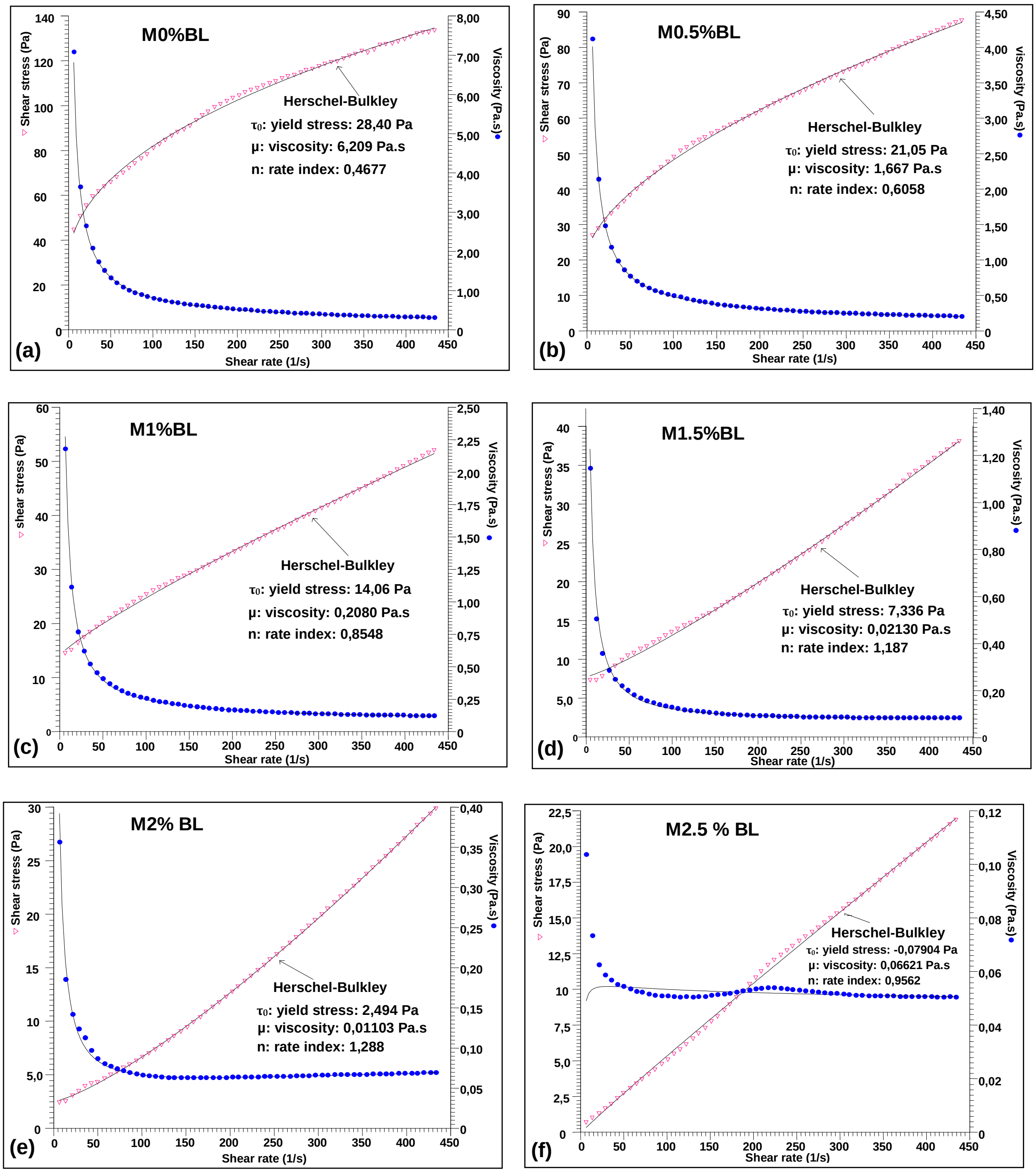

Fig. 5. Curves of Shear stress and viscosity versus shear rate flow for the 0.35 W/C cement pastes investigated at various black liquor concentrations. (a)M0%BL; (b)M0.5%BL; (c)M1%BL; (d)M1.5%BL; (e)M2%BL; (f)M2.5%BL

Tests on concrete

The effectiveness of black liquor in preparing self concrete is checked by using a replacement of water with 2%BL. In order to compare the results, concrete is made using commercially available lingo-sulphate superplasticizer also. For this purpose, we used the Dreux Gorisse method for formulation mixing.

Table 8 summarizes the mix proportions used for production of the concretes. The original concretes were designated in (CW), the concretes with superplasticizer admixture (SIKAFLUID®-300) designated (C2%SF300), whereas the concretes with 2% of black liquor designated (C2%BL). The water/ cement ratios (W/C) of concretes are similar to those for the concretes (W/C=0.35). In order to achieve a similar degree of workability for all three types of concrete.

Table 8. *Mix proportion of concrete*

Mix designation	Mix proportions (kg/m^3)				Water (l/m^3)	BL (l/m^3)	SIKAFLUID®-300 (l/m^3)
	Cement	Sand	Aggregate 3/8	Aggregate 8/15			
CW	400	660	255	868	140	--	--
C2%SF300	400	660	255	868	140	--	8
C2%BL	400	660	255	868	140	8	--

Slump test

The workability of concrete mixtures with a replacement of 2%wt Cement by black liquor and superplasticizer (SIKAFLUID®-300) determined in accordance with the provisions of the Algerian standard NA 431[47]. The Table 9 shows the variation of the slump test (Abrams cone test) as a function of time (minutes) of the three formulations. It was observed that there was an increase in workability by increasing the slump values of the sample (C2% BL) relative to the control (CW). Slump increasing is compared in Table 9, which shows that concretes (C2%SF300) and (C2%BL) produced a high slump until 30 minutes, whereas cement (CW) had a slump less weak compared to two other concretes until the hardening at (180 minutes). The fluidity of the concrete grout decreases with time due to the hydration phenomenon of the cement constituents [48–50].

Table 9. *Slump test of concrete*

Time (min)	Slump test (mm)		
	CW	C2%SF300	C2%BL
0	73	180	165
30	61	138	126
60	49	98	87
90	35,5	65	51
120	21,2	42	31
150	7,8	22	13
180	0	3	6

Obviously, the rate of slump loss for mixtures (C2%SF300) and (C2%BL) is higher than that of a mixture (CW).

Slump of (C2% BL) is similar to that of the mixture (C2% SF300), and this explains the same role that black liquor plays in the fluidity of the mortar and thus confirms the rheological behavior illustrated in Fig. 5. The black liquor acts as a dispersing agent by neutralizing the electrostatic charges of the concrete mixture, especially the cement. This neutralization minimizes agglomeration of the solid particles allowing them to mix better with water [51].

Compressive strengths of concrete

Compressive strength of concrete is one of the most important and useful properties. As a construction material, concrete is employed to resist compressive stresses. While, at locations where tensile strength or shear strength is of primary importance, the compressive strength is used to estimate the required property.

Table 10. *Compressive strengths of concrete*

	Compressive strengths (MPa)				
Mix designation	2 days	7 days	14 days	28 days	90 days
CW	6,53	17,95	24,89	43,056	47,23
C2%SF300	7,86	19,83	28,45	47,96	53,21
C2%BL	6,93	18,036	26,67	46,35	53,69

Compressive strength tests were conducted on cured cube specimen provisions of the standard (NF EN 12930-3) [52] (150mm.150mm.150mm) at 2,7,14, 28 and 90 days age using a compression testing machine of 300 tons capacity. The load was then slowly applied to the tested cube until failure. Table 10 show the average value of concrete cube compressive strength in different ages for concrete mix and mixes containing (2% of Water content) black liquor (BL) and superplasticizer (SIKAFLUID®-300).

The compressive strength of the hardened concrete pastes was generally increased with curing time up to 90 days, as expected from the continuous hydration process. The apparent porosity decreased gradually and the compactness of samples improved, hence the bulk density increased [53].

The effect of 2% BL addition was beneficial in concrete. It might be explained by activation of the —OH- groups present in the black liquor (BL).

The (BL) solution in the hydration water led to the formation of electrostatic repulsive forces between cement particles which become negatively charged by the adsorption. This will reduce the attraction between the cement particles, preventing their flocculation or agglomeration and then creating a well-dispersed system. Consequently, the compactness will enhance and direct benefits are expected on the mechanical resistance.

The results of compressive strength obtained indicate a relatively slow rate of hydration (compressive strength values very close for the three concretes tested) during the early ages of hydration up to 14 days, followed by increasing compressive strength up to 28 days of hydration. These results are attributed to retarding effect of setting time of black liquor leading to the formation and later accumulation of hydration products, namely as calcium silicate hydrates (CSH-I, CSH-II), which act as a good binding centers between the remaining unhydrated cement grains.

On the other hand the rate of increase in the compressive strength values during the period from 7 to 28 days is due to the fact that the initially formed hydration products shielded the remaining unhydrated parts of cement grains leading to a quick rate of hydration during this period [33] [42].

The (C2%BL) hardened pastes showed nearly the same trend as in case of (C2%SF300), but with a notable lower values of compressive strength especially during the early ages of hydration (up to 14days). After 28 days of hydration specimens made from (C2%BL) showed a slight higher value of compressive strength than (C2%SF300) and showed the highest strength value among all tested specimens after 90 days. Either a compressive strength gain of 10% at 28 days and 12% at 90 days.

The compressive strength of concrete after curing showed growth trends as time increased, which indicated that BL was advantageous for the improvement of the long-term compressive strength of concrete though retarding effect was observed in the initial stage of cement hydration.

CONCLUSIONS

The use of black liquor isolated from date palm wood has a very important scientist and economic interest. Black liquor is considered as a low cost admixture to increase the workability and compressive strength of concrete.

The results of this research show that black liquor produced from date palm trunk noticeably increases the workability of concrete with maximum performance at 2% water replacement by black liquor.

Effects of dosage of black liquor on the rheological properties of mortar and the rheological curves which have been studied to determine the saturation dosage. The yield stress and the plastic viscosity stress were dramatically decreased at dosage of 0.5–2 wt. %, compared with the sample without BL.

Both the Herschel-Bulkley and Bingham models fit the experimental data from the viscometer study satisfactorily. It is observed that the nature of flow in superplasticized paste varies slightly with the dosage of black liquor, as follows. At lower dosages, nonlinear shear thinning is generally observed; around the saturation dosage the response follows the Bingham model; and at higher dosages, there may be some shear thickening.

The yield stress values obtained with both the models have the same trend with respect to black liquor dosage, though the values from the Bingham model tend to be higher at smaller black liquor dosages. Even though shearthickening nature of paste is better represented through the Herschel-Bulkley model, the Bingham model represents the behavior of normal pastes well.

An increase in black liquor dosage leads to a decrease in the yield stress, plastic viscosity, and an increase in minislump spread, as long as the dosages are below the saturation point. Beyond the saturation dosage (2% of Water content), these parameters are practically constant.

The values of compressive strength for hardened pastes made of in 2% black liquor showed a notable lower values especially during the early ages of hydration (up to 14 days), and showed a comparable and/or higher values after 28 days of hydration as compared to the control concrete (CW).

Black liquor has similar performance compared to the commercially available SIKAFLUID®-300 admixture for making self-compacting concrete and it is observed that processed black liquor is effective in producing self compacting concrete.

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