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Manufacturing of Pulp from Wheat Straw (*Triticum aestivum* L.) by KOH-Air Method

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Abstract

Paper manufacturing is a very high water use per ton industrial sector. Chemicals and organic and inorganic substances which pass through black solution from raw material during cooking may cause pollution. Generally, NaOH method is used to manufacture paper pulp from cereal straw. Since, sodium increases water salinity in black liquor which was a residue from paper pulp processes and it must be removed. Black liqour treatment increases the time and cost of operations. For these reasons it has become imperative to search for ways to dispose of the black liquor without performing purification. For this purpose, the alkali selected for cooking should not cause salinity to the soil. In order to produce pulp, KOH was used which is a weaker base than NaOH. Because air has bleaching characteristic, KOH-Air cookings were performed. On the other hand, if potassium is used correctly it will be a considerable nutrient for plants. In this study, the black liquor obtained was strong base having mean pH as 12. The optimum pulp manufacturing conditions were temperature, time and KOH ratio were determined as 120°C, 60 min and 18% KOH. It has seen that pulp and paper quality of KOH method compete par with traditional NaOH method pulp and paper using wheat straw.

Keywords: Pulp, paper, KOH-Air method, wheat straw.

Buğday Saplarından (*Triticum aestivum* L.) KOH-Hava Metodu İle Kâğıt Hamuru Üretimi

Öz

Kâğıt üretimi ton başına üretimde oldukça yüksek su kullanımı olan bir endüstriyel alandır. Pişirme sırasında hammaddeden siyah çözeltiye geçen kimyasallar ve organik ve inorganik maddeler kirliliğe neden olabilir. Genellikle, ekin saplarından kâğıt hamuru elde etmek için NaOH metodu kullanılır. Kâğıt hamuru proseslerinden arta kalan sodyum atık sularda tuzluluğa neden olduğundan uzaklaştırılmalıdır. Siyah çözelti arıtma işlemi zaman ve maliyet artışına neden olmaktadır. Bu nedenlerden dolayı siyah çözeltiyi arıtmadan uzaklaştırmanın yollarını aramak önemlidir. Bu amaçla pişirme için seçilen alkali toprakta tuzluluk yapmamalıdır. Kâğıt hamuru üretmek için NaOH'tan zayıf bir alkali olan KOH seçilmiştir. Hava ağartıcı özellikte olduğundan, KOH-Hava pişirmesi yapılmıştır. Eğer potasyum doğru kullanılırsa bitkiler için önemli bir besin kaynağıdır. Bu çalışmada, elde edilen siyah çözelti pH ortalaması 12 olan güçlü bir bazdır. Optimum hamur üretim şartları sıcaklık, zaman ve KOH oranı olarak sırasıyla 120°C, 60 dak. ve %18 KOH olarak tespit edilmiştir. KOH metodu ile elde edilen hamur ve kâğıtların kalitesi geleneksel NaOH metodu ile buğday saplarından üretilen hamur ve kağıtlarla başabaş rekabet edecek seviyede olduğu görülmüştür.

Anahtar Kelimeler: Kağıt hamuru, kağıt, KOH-hava metodu, buğday sapı.

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1. Introduction

For a livable world, industrial productions should not distort the balance of nature. All of the materials changing natural structure of the environment are classified by pollutants. However, in reality, narrower classification may be more useful. Environmental protection agency (EPA) roughly classifies pollutants with eight different types. These are oxygen consuming materials, materials that cause sickness, synthetic organic compounds, agricultural fertilizers, inorganic chemicals and minerals, sediments, radioactive compounds and thermal waste (Springer 1993). Three classes of inorganic chemical compounds and minerals cause significant amount of pollution in pulp and paper mills. These are; acids, alkali and heavy metals (Miner and Unwin, 1991). Chen et al., (2017) have pointed out that more effective washing of waste water enhances pollution control the pollutant discharges from pulp and paper industry. In the beginning of 1970s first laws were established in Canada about the regulations of discharging the waste water from the pulp and paper mills to rivers and streams.

Pulp and paper mill waste water cannot be discharged without treatment. Stavropoulas (1988) indicates that during incineration, poisonous gasses were transferred to atmosphere and heavy metals were remained in the ash. On the other hand, ash is another type of hazardous waste (Yang et al., 2015). For this reason, incineration is not suitable and more environmentally conscious approaches are essential for sludge treatment.

Mostly fine material is bonded with alkaline method and waste water is generally cleaner than acidic methods (Crouse and Douglas, 1991). Developments in pulping, lesser pollution, lower production costs cause the transition from acidic methods to alkaline methods. For this reason, an alkaline method was used in our study.

Caustic soda method which is traditional method is used in the alkaline pulping form creal straw. Nevertheless, Neal et al., (2005) indicated that sodium in the black liquor caused salinity in water and soil. Waste water contained sodium make adverse effect organisms. For this reason, without recovering these waste water are not unleashed sea and landfill.

In the alkaline cooking OH – ion ratio is effect to delignification (Zou et al., 2000). KOH is a weaker base than NaOH. While Na+ ion is increased the salinity soil and water, K+ ion is an important fertilizer for plants. Gençer et al., (2006) indicated that black liquor which was 12 pH by using KOH method produced pulp titrate with H2SO4 and P2O5 dilute concentration can be used fertilizer. Therefore, the KOH method is preferred over the classical NaOH method.

Cereal straw rather can be cooked easily than wood. For example, Deniz et al., (2004) the temperature of cooking was determined as 120 ºC in the production of paper by the method of NaOH from wheat stalks. On the other hand, Istek and Özkan (2008) and Gülsoy et al., (2015) reported that the cooking temperature in the production of paper by the aspen and pomegranate Kraft method is 170 ºC. For this reason, this study has been carried out with the conclusion that instead of wood, nonwood can be used.

2. Materials and Methods

Wheat is a major food source in the world and belongs to grass family of *Triticum species* (Lupton 1987). For this reason, in this study wheat (*Triticum aestivum* L.) straws were used. Samples used in the experiment were obtained from Bartın Province, located on the coast of the Western Black Sea region in Turkey. They were obtained at an altitude of 50 meters from the South exposure. Afterwards, the moisture content of the wheat straw stalks was determined based on the oven-dry and air-dry weights. To determine the chemical properties of wheat straw the samples were ground in a Wiley mill according to the TAPPI T 257 cm–02 standard. This was followed by screening to the 60 mesh size, and the resulting material was used for chemical analysis. TAPPI T 204 cm–97 standard was used to determine the material's solubility in alcohol. The TAPPI T 203 cm–99 standard was used to determine cellulose; the TAPPI T 222 om–02 standard was used to determine the lignin content; the TAPPI T 207 cm–99 standard was used to determine the material's solubility in cold and hot water. The wheat straw stalks were cut 5 cm length for the KOH cooking process. Dry sample weights of 500 g wheat straw stalks were prepared and kept in polyethylene bags in the absence of air. Cooking process was done in 15 liter capacity, electrically heated, bearing 25 kg/cm^2 pressure, laboratory type rotational chamber at the rate of 2 minute rpm. Dry air which its pressure 8 kg/cm^2 was loaded with the help of a condenser before the cooking process. One cooking was carried out in the most optimum conditions of the 27 cookings performed before the air was loaded. In order to obtain the black liquor a special collection unit was placed under the screen and after screening the black liquor, the pulp was obtained by hand and roller over the screen. pH measurement at 20ºC and alkali consumption with 0.1 N HCl neutralization of black liquor was carried out.

Paper made from the pulp 50 ºSR were determined the brightness (TAPPI T 525 om-02), opacity (TAPPI T 519 om-02), tearing index (TAPP T 414 om-98), burst index (TAPPI T 403 om-02), and breaking length (TAPPI T 494 om-01) of each of the papers. The experimental papers were subjected to the following tests after they are conditioned in an environmental test chamber with 65% relative humidity at a temperature of 23 ± 1 °C for 24 hr according to the TAPPI T402 sp–03 standard.

3. Results and Discussion

Table 1. Chemical and physical features of wheat straw (Triticum aestivum L.)

Properties and solution (%)	Mean	Variation coefficient	Minimum value	Maximum value
Holocellulose	74.40±0.25	0.34	74.15	74.65
Cellulose	48.87±0.25	0.51	48.60	49.10
Lignin	15.80±0.13	0.86	15.69	15.95
Ash	7.09±0.06	0.92	7.02	7.15
Alcohol-Benzene Sol.	5.46±0.06	1.22	5.40	5.53
%1 NaOH Sol.	40.96±0.16	0.39	40.80	41.12
Hot Water Sol.	12.49±0.34	2.77	12.16	12.85
Cold Water Sol.	7.75±0.06	0.84	7.69	7.82

Deniz et al., (2004) found the holocellulose value of wheat straw to be 74.50% and the lignin value to be 15.30%. Gümüşkaya et al., (2007) found the holocellulose value of hemp (Cannabis sativa L.) bast fibers to be 86.93%. The holocellulose value determined in this study was 74.40, while the lignin value was 15.80%; these values were similar to the wheat straw values given above. TAPPI T236 om-99 standard was used to measure kappa number. Viscosity was measured according to SCAN-cm 15-62 standard.

Table 2. Some properties of the pulp produced from wheat straw, black liquor and cooking conditions.

C. No	Cooking conditions			Screened yield (%)	Total yield (%)	pH	Kappa No	Viscosity (cm^3/g)
	KOH (%)	Temperature (°C)	Time (min.)					
1	14	110	60	38.05	56.35	12.3	40.21	896
2	14	110	90	39.52	56.52	120	36.24	851
3	14	110	120	40.68	55.35	11.9	34.00	832
4	14	120	60	40.55	55.71	12.0	38.20	853
5	14	120	90	42.15	56.16	11.9	35.61	831
6	14	120	120	42.73	55.15	11.7	33.05	810
7	14	130	60	40.01	53.31	11.5	37.34	821
8	14	130	90	40.95	52.98	11.3	33.02	801
9	14	130	120	41.90	53.25	11.5	32.71	790
10	16	110	60	41.14	55.97	12.1	36.23	850
11	16	110	90	41.30	53.49	120	35.41	821
12	16	110	120	41.81	54.76	10.7	35.03	805
13	16	120	60	42.06	56.56	11.9	33.25	802
14	16	120	90	43.24	55.39	11.3	33.72	780
15	16	120	120	42.66	52.66	10.9	32.10	761
16	16	130	60	41.48	53.62	10.6	33.03	778
17	16	130	90	40.86	52.07	10.8	32.22	761
18	16	130	120	40.68	51.83	10.4	30.04	749
19	18	110	60	41.99	54.32	11.6	30.91	801
20	18	110	90	43,89	55.80	114	31.52	783
21	18	110	120	43.20	55.20	11.5	30.60	771
22*	18	120	60	45.35	55.40	11.0	30.57	765
23	18	120	90	43.98	56.57	11.3	29.83	749
24	18	120	120	44.36	53.63	11.0	28.31	728
25	18	130	60	43.08	52.74	10.5	30.32	770
26	18	130	90	42.86	51.98	10.2	29.10	741
27	18	130	120	41.50	49.64	10.3	27.41	702

Air pressure:8 kg/cm^2; Liquor/Wheat straw-:5/1, C.No: Cooking No

When evaluating a paper pulp obtained by any method, the highest rate of pulp yield, the lowest value of the Kappa number and the highest value of viscosity are the essence. Humidity measurement and screened yield values were measured according to TAPPI T 220 cm-86 standard. In order to obtain experimental papers, pulp was beaten according to TAPPI T 200 0m-89 standard until it reaches to 50 ± 2 °SR degrees.

Table 3. Physical, mechanical, and optical tests conducted for wheat straw paper produced by 50 SR°

C. No	Cooking conditions KOH (%)	Temp. (°C)	Time (min)	Breaking length (km)	Burst index (kPam^2/g)	Tear index (mNm^2/g)	Brightness (%MgO)	Opacity (%)
1	14	110	60	6.477	4.21	4.38	27.24	92.2
2	14	110	90	7.213	4.43	4.38	27.40	94.1
3	14	110	120	6.250	4.20	4.90	28.34	93.9
4	14	120	60	6.461	4.38	4.92	25.12	96.4
5	14	120	90	8.543	4.96	4.99	25.21	93.5
6	14	120	120	8.714	4.74	5.54	25.46	93.8
7	14	130	60	8.091	4.66	5.52	24.29	95.5
8	14	130	90	6.628	4.53	5.67	24.69	96.1
9	14	130	120	7.595	4.74	5.46	23.03	95.9
10	16	110	60	7.096	4.44	4.69	28.77	92.7
11	16	110	90	7.362	4.66	4.89	29.48	90.9
12	16	110	120	7.134	4.76	5.57	27.61	92.7
13	16	120	60	6.283	4.35	4.82	27.85	93.5
14	16	120	90	7.146	4.48	5.40	27.37	94.5
15	16	120	120	7.125	4.36	4.59	27.09	92.5
16	16	130	60	6.509	4.55	4.59	27.86	95.2
17	16	130	90	6.835	4.23	5.06	25.86	96.6
18	16	130	120	6.843	4.53	5.03	25.13	95.2
19	18	110	60	6.900	4.72	5.54	27.27	92.4
20	18	110	90	7.797	4.97	5.46	30.20	91.0
21	18	110	120	7.449	4.65	4.85	26.78	88.7
22	18	120	60	6.592	4.70	5.37	27.,83	92.8
23	18	120	90	7.123	4.72	5.34	29.34	91.7
24	18	120	120	6.780	4.36	4.22	30.78	93.5
25	18	130	60	7.427	4.59	5.07	27.26	95
26	18	130	90	7.255	4.83	4.76	26.92	95.4
27	18	130	120	7.255	4.63	4.47	26.94	95.6

Break length is highest at 90 minutes, temperature 120 °C and 14% KOH. When the burst index cooking times are evaluated among themselves, it is highest when 90 minutes is taken (4.64 kPa.m^2/g). Cooking temperatures are highest at 130 °C when examined independently of other variables. However, the difference between the values at 120 °C at 5% significance level is not found significant. By increasing the temperature from 120 °C to 130 °C, the efficiency decreased, the viscosity decreased and the whiteness value decreased in all cooking. While making paper for general use from a raw material, the issue of which properties of the paper should be high and which should be low can be conflicting and confusing. For example, sanitary papers are expected to have high water absorption capacity, and packing papers are expected to have low absorption capacity. In addition, since air permeability and paper thickness changes according to the features of the paper that is produced, the determination of optimum conditions is relative. However, while determining the optimum conditions in making pulp, pulps that have the highest yield and the lowest kappa numbers are preferred. It has become a tradition to prefer and accept pulp that produces paper with the best mechanical and optical values. Acquiring all of the desired features in a single pulp is, for the most part, impossible. Thus, it is very difficult to identify optimum cooking conditions. In our study, the highest values of breaking length, brightness, burst index, tearing index, opacity, whiteness, and surface smoothness at 50 SR° and the values in which the difference between those values is not statistically significant at 5% were taken into account, and a scoring table was developed in order to determine the optimum condition. Moreover, the highest values and the value(s) in which the difference between those values is not statistically significant at 5% were each graded as 1, while all of the remaining values were graded as 0. According to the results of the Tukey test, the most suitable conditions are the paper pulp and paper produced by the KOH-air method from wheat stalks (Table 4).

Table 4 Physical and mechanical properties of paper pulp and paper obtained by using KOH-air method

Pulp-Paper Properties	Coking Parameters								
	Temperature (°C)			Time (min)			KOH Ratio (%)		
	110	120	130	60	90	120	14	16	18
Screened Yield (%)	0	45.35*	0	45.35*	0	0	0	0	45.35*
Kappa Number	0	0	27.4*	0	0	27.4*	0	0	27.4*
Viscosite (cm^3/g)	896*	0	0	896*	0	0	896*	0	0
Breaking Length (km)	0	7.19*	7.16	0	7.32*	0	7.33*	0	0
Burst Index ($kPa.m^2/g$)	4.55	4.56	4.59*	0	4.64*	0	0	0	4.68*
Tear Index ($mN.m^2/g$)	4.96	5.02	5.07*	4.96	5.10*	4.99	5.08*	4.96	5.01
Brightness(% MgO)	28.12*	0	0	27,05	27.38*	0	0	0	28.14*
Opacity (%)	0	0	95.53*	93.91*	93.73	0	94.58	0	0
Score	4	4	5	5	5	2	4	1	5
Corrected score	4	5	4	6	4	2	4	1	5

In the bleaching process, the level of bleaching of the pulp increases as the kappa number decreases. Therefore, the lowest value is essential. While writing the kappa numbers in the table, the lowest values and the value(s) in which the difference between those values is not statistically significant at 5% were each graded as 1, while all of the remaining values were graded as 0. The tear index is highest at 130 °C when the temperatures are examined. However, the difference between the value at 120 °C and the 5% significance level is not significant. Rising of the temperature from 120 °C to 130 °C resulted in a deterioration in the other properties of the pulp and paper as well as an burst index value. For these reasons, the cooking temperature can be 120 °C to save energy. Regardless of other variables, the whiteness value is highest in 90 minutes when cooking time is examined (27.38). However, the difference between the values of 60 minutes (27.05) is not significant at the 5% significance level. For this reason, the cooking time can be taken 60 minutes for the optimum whiteness value. At the end of these regulations the score of 130°C in the score made in Table 5.1 falls from 5 to 4. The temperature of 120°C rises from 4 to 6. Likewise, the score of 90 minutes is reduced from 5 to 4, while the score of 60 minutes is increased from 5 to 6. When the KOH ratios are evaluated among themselves, the score of 18% is highest.

According to these results, for the 27 cooking test plans for the production of paper pulp by KOH-air method from wheat stalks;

Temperature: 120 °C
Cooking time: 60 min.
KOH ratio: %18 is the optimum cooking condition.

4. Conclusion

Wheat straw use in paper production goes back to very early times. However, enterprises still have been facing serious problems in chemical recovery units. Non-cellulosic wood compounds get into black liquor either in pure form or complex compounds (Freeman, 1995). On the other hand, wheat straw black liquor, having silica which is occurred after cooking, increases viscosity of the black liquor, and makes chemical recovery more difficult. Moreover silica clogs the screens and causes serious problems in production. Generally waste products are tried to be taken under control by purifying, incineration, making compost and storage.

In this study, the KOH method was used. Trying other chemical, semi-chemical, and mechanical methods will help to make more precise decisions on the advisability of using wheat straw for pulp production. The cost of transporting the waste solution in liquid form can be increased. For this reason it will be beneficial for the water to be removed at certain times. Dehydration of the sludge may cause the dissolved compounds go away with the

water. KOH black liquor obtained from the pulp production may be a sustainable nutrient source for plants. This waste should be utilized in the plant growing in order to provide income for pulp manufacturers.
In our study, the screened yield, tear index and burst index values are higher than those of Deniz et al., (2004). For this reason, it can be said that the KOH method is an acceptable process when it is based on accepted sodium hydroxide (NaOH) method in the paper industry. It has been observed that air loading has a positive effect on the properties of both pulp and paper compared to the cooking without air loading in optimum cooking conditions.

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