The Effects of Cooking and Bleaching on Organic Chemical Compounds in CMP Pulp and Newsprint

Ramin Vaysi

Yellowing and brightness stability of newsprint are very important phenomena mostly dominated by residual organic compounds. In this research, effects of cooking and bleaching on organically chemical compounds in CMP pulp and newsprint were investigated. For this purpose, samples were chosen randomly from chips, CMP pulp after cooking, after bleaching, and in newsprint produced in Mazandaran Pulp and Paper Mill (in north of Iran). At first stage, the paper flour was provided, and then the quantity of extractives was measured in percent by TAPPI standards. The GC diagram was used for identification of the compounds. The results of GC analysis showed that in chips, CMP pulp after cooking, after bleaching, and in newsprint paper, were 90, 76, 68, and 58 compounds, respectively. The common and important chemical components in the samples were benzaldehyde, dodecane, bibanzyl, 1,2-benzendicarboxylic acid, didutyl phthalate, and bis (2-ethylhexyl) phthalate. The benzaldehyde (32.56%), bis (2-ethylhexyl) phthalate (6.98%), gamma-sitosterol (4.84%) were the most abundant compounds, and the dodecanoic acid (0.14%), decane (0.18%), xylene (0.19%), and benzene,1-methyl-4-phenylmethyl (0.2%) were also present.

Key words; Cooking; Bleaching; Chemical Compounds; Newsprint and CMP Pulp

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INTRODUCTION

About 52,000 t/y newsprint is produced from CMP pulp in Mazandaran Pulp and Paper Industries Company (located in north of Iran). The newsprint is susceptible to photo-oxidative reactions, which cause the pulps to become discolored and to revert to lower brightness. Some extractives compounds have been proposed or considered as initiators or the main cause of the yellowing in high-yield and mechanical pulps; thus their extraction and identification are very important.

The rapid increase in the population of developing countries and the demand for different kinds of paper and paper products has led to greater and more diverse utilization of non-wood fiber resources. It has been estimated that more than 21 million tons of virgin pulp is produced from non-woody fiber resources (Khakifirooz *et al.* 2013). Lignin-rich mechanical pulps are susceptible to photo-oxidative reactions, which cause these pulps to become discolored and to exhibit brightness reversion (Vaysi and Mirshokraie 2007).

Newsprint paper has shown the largest amount of yellowing when exposed to polychromatic irradiation in the wavelength region of 330 to 385 nm (UV-A region). Newly-formed phenolic and carboxylic groups from quinines radicals during photo-yellowing were considered to be responsible. Extractives identified in such pulp have been proposed or considered as initiators or the main cause of yellowing in high-yield and mechanical pulps (Andrady and Searle 1995).

In long-term aging, DTPA spray has been shown to have considerable effect on the stability of brightness, improving the durability of the hornbeam CMP against optical deterioration in subsequent accelerated irradiation aging (Vaysi *et al.* 2007).

Experiments with untreated and acetylated aspen chemi-thermo-mechanical pulp (CTMP) exposed to argon, air, and oxygen atmospheres showed that the degree of photo-yellowing of the untreated CTMP decreased when the air in the surrounding atmosphere was replaced with oxygen-free argon. The results indicated that atmospheric oxygen was not of sole importance for the light-induced discoloration or that the trace amount of oxygen was necessary to cause discoloration (Paulsson *et al.* 2001). In long-term aging, diethylenetriaminepentaacetic acid (DTPA) spray has been shown to have considerable effect on the stability of brightness and improving the durability of the hornbeam chemi-mechanical pulp (CMP) against optical deterioration in subsequent accelerated irradiation aging (Vaysi and Mirshokraie 2007).

Several factors and structural elements, as follows, have been proposed or considered as initiators of the main cause of the yellowing in high-yield and mechanical pulps: oxygen, α-carbonyl structures, lignin double bond structures, singlet oxygen, various radicals, phenolic groups (catechols), ortho-quinones, para-quinones such as methoxy-p-benzoquinone, lignin β-O-4 structures, hydroquinones, and stilbenes formed from the phenylcoumaran-type entities (Forsskahl and Tylli 1993).

The quinone structures and quinone precursors such as hydroquinones and catechols are important factors in the photo-yellowing process in acetylated ground wood pulps (Ek *et al*.1992). The catalytic activity of Mn^{2+} and Mn^{3+} was shown in hydrogen peroxide decomposing studied using DTPA as the only stabilizer. It was found that addition of DTPA to a Mn^{2+} containing system is more effective than its addition to a Mn^{3+} containing system. The effect of pH on using DTPA to decrease Mn induced peroxide decomposition has been discussed (Qiu *et al*. 2003). The average of extractives in natural and planted cypress tree are 7.52 and 2.57 percent respectively. There are specified 14 compounds in natural and 12 compounds in planted cypress tree. Of these, the compounds isophyllocladene, 9-octadecenamide, cinnamaldehyde-2-hexyl, bourbonanone, and 1h-naphtho[2,3-c]pyran-3-acetic acid have been shown to be very important relative to its durability (Vaysi 2007). In this study, the effects of cooking and bleaching on organic chemical compounds in chemi-mecanical pulp and newsprint were investigated.

EXPERIMENTAL

Pulp

In this research, Horn Beam chips were chosen randomly from chips pile at Mazandaran Wood and Paper Mill (MWPM) and cooked under CMP conditions (l/w:7 ,SO_2:116 g/L ,NO_2:106 g/L ,sodium sulfite:20% and for 60 minutes in 160 ^oC), and pulps were prepared at the yield of 85% (Vaysi *et al.* 2007).

Pulp Bleaching

A portion of the pulp was bleached using hydrogen peroxide and DTPA as chelating agent according to the method proposed under following conditions: Hydrogen peroxide: 3%, sodium hydroxide on hydrogen peroxide ratio: 0.7% , DTPA charge: 0.3%, Na_2SiO_3: 3%, pulp consistency:12%, time: 1 hour, and temperature: 75 ^oC. Then, pulps

were refined to freeness of 300 mL (CSF) by PFI Mill. Some of the pulps were bleached with sodium dithionite. Then 60 gr/m^2 handsheets were made from bleached and unbleached pulp according to TAPPI T 205 om-88 before acetylating (Vaysi and Mirshokraie 2007).

Sampling

In this study, the chips, CMP pulp after cooking, the same after bleaching, and newsprint samples were chosen randomly from paper newsprint produced in Mazandaran Pulp and Paper Mill (MWPI) in north of Iran (Sari City). Then, samples of flour provided and flour extractives were measured by TAPPI standards.

Essential Flours Extraction

Samples of flour were washed by acetone, and extractives residue was added to a BSTFA reactor, with samples kept in a Ben Marry Bath at 70^{o}C for an hour, and they were analyzed by GC/MS. The pure extractives obtained were separated and dried by nitrogen gas to give pale red colored extracts in 10 and 12% yields from wood flour. For identification of extract, about 1 mg solid extracts was obtained, then mixed with 30 micro liter BSTFA + 1% TMCS reagent and about 15 micro liter pyridine inside a tube test.

Gas Chromatography-Mass Spectrometry

The samples were kept in a Ben Marry Bath at 70^{o}C for an hour, and they were analyzed using GC/MS on an HP 6890 Gas Chromatograph, equipped with a split/split less injector and a 5973 Mass Selective Detector (MSD). The column oven was programmed as follows: Chromatography was performed on a HP-5MS capillary column (SGE, 30 m, 0.25 mm). As the carrier gas, helium with a flow of 1 mL/min and a temperature program between 60 and 260 °C, with increasing temperature at a rate of 6 °C/min.

Identification of Compounds

A GC diagram was used for identification of compounds from which the abundance and retention time of each compound is identified, and the calculation of quartz index and Adams table is shown. The retention indices were calculated for all volatile constituents using a homologous series of C9 to C19 n-Alkanes (Vaysi 2014),

$$\text{Quartz Index} = 100n + 100\,(t_{rx}-t_{rn})/(t_{rn+1}-t_{rn}) \quad (1)$$

where n is the carbon number of normal Alcan, t_{rn+1} is the retention time of the unknown compound, and t_{rn} is the retention time of normal Alcan.

RESULTS AND DISCUSSION

Newsprint is susceptible to photo-oxidative reactions, which cause the pulps to become discolored and to suffer from brightness reversion. Some organic compounds have been proposed or considered as initiators or the main cause of the yellowing in high-yield and mechanical pulps, so that its extraction and identification can be considered as very important. The results of this study showed that the average of extractives was 10.32% percent in chips. Among 90 compounds found to be present in the chips, the

following were judged to be important: benzaldehyde (13.29%), xylene (3.39%), bibanzyl (4.8%), benzenemethanol (4.75%), gamma-sitosterol (5.2%), beta-sitosterol (0.36%), bis(2-ethylhexyl)phthalate(1.48%), 1,2-benzendi-carboxylic acid (4.09%), benzyl ethanol (0.96%), 9,12-octadecanoic acid (5.24%), didutyl phthalate (0.68%), dodecane (1.85%), and tetradecane (0.95%). Components in chips for CMP pulp production are shown in Table 1. There were almost 150 compounds in false acacia wood, of which the following were classified as being important: resorcinol (19.47%), 1,3-benzendiol (6.92%), stigma sterol (5.45%), 9-octadecenoic acid (3.55%), 1h-imidazol (3.08%), gamma-sitosterol (2.77%), and gamma-terpinene (0.22%). There were 37 compounds found in sweet locust wood, of which 1,2-benzenedicarboxylic acid (90.38%), stigmast-4-en-3-one (2.62%), resorcinol (1.07%), silicon grease (0.73%), gibberellins a_3 (0.14%), and phenol (0.09%) were important compounds. Resorcinol and 1,2-benzenedicarboxylic acid were both present in sweet locust and false acacia woods. It seems that probably the presence of a high percentage level of resorcinol (20%) in sweet locust and of 1,2-benzenedicarboxylic acid (90.38%) in false acacia is an important factor for durability of these species (Vaysi 2014).

The results of this study showed the average of extractives was 12.92% percent in CMP pulp after cooking. Out of the 76 compounds specified to be in CMP pulp after cooking, the following were judged to be important: benzaldehyde (15.27%), bis(2-ethylhexyl)phthalate (2.32%), gamma-sitosterol (2.61%), beta-sitosterol (4.63%), benzyl alcohol (1.8%), 9,12-octadecanoic acid (1.54%), dibutyl phthalate (0.74%), dodecane (1.58%), tetradecane (0.95%), bibanzyl (0.39%), and 1,2-benzendicarboxylic acid. Several factors and structural elements, as follows, have been proposed or considered as initiators of the main cause of the yellowing in high-yield and mechanical pulps: oxygen, α-carbonyl structures, lignin double bond structures, singlet oxygen, various radicals, phenolic groups (catechols), ortho-quinones, para-quinones such as methoxy-p-benzoquinone, lignin ß-O-4 structures, hydroquinones, and stilbenes formed from the phenylcoumaran-type entities (Forsskahl 2000; Carter 1996).

The results of this study showed the average of extractives was 7.2% percent in CMP pulp after bleaching. Of the 68 compounds specified to be present in CMP pulp after cooking, the following were classified as being important: benzaldehyde (45.71%), hydrochloric acid (1.99%), dodecane (0.32%), bibanzyl (4.55%), propanoic acid (2.15%), bis(2-ethylhexyl)phthalate (8.79%), 9-octadecanoic acid (6.68%), didutyl phthalate (1.3%), tetradecane (0.28%), bibanzyl (4.55%), and 1,2-benzendicarboxylic acid (1.28%), as shown in Fig. 1.

Newsprint papers are susceptible to photo-oxidative reactions, which cause the pulps to become discolored and to revert in brightness. Some extractive compounds have been proposed or considered as initiators or the main cause of yellowing in high-yield and mechanical pulps. The CMP pulps likewise are susceptible to photo-oxidative reactions, which cause these pulps to become discolored and to exhibit brightness reversion. New phenolic and carboxylic groups are formed from quinone radicals during photo-yellowing and long-term accelerated light aging; *o*-quinones can be oxidized to muconic acids by peroxide or can be reduced to catcheols by dithionite reductive bleaching. These new groups could form chromophoric groups in combination with metallic ions. Such factors may account for the observed unfavorable effects on pulp brightness, including brightness reversion (Ek *et al.* 1992).

The results of this study showed the average of extractives was 6.92% percent in newsprint. Out of the 58 compounds identified to be present in newsprint, the following were judged to be important: benzaldehyde (32.56%), bis(2-ethylhexyl)-phthalate

(6.98%), gamma-sitosterol (4.84%) , n-hexadecanoic acid (4.59%), bibenzyl (3.82%) and octadecanoic acid (3.55%), dodecanoic acid (0.14%), decane (0.18%), xylene (0.19%), benzen,1-methyl-4-phenylmethyl (0.2%), and tetradecane (0.37%) (Figs. 2 and 3). The newsprint exposed to polychromatic radiation showed the largest amount of yellowing when exposed to irradiation in the wavelength region of 330 to 385 nm (UV-A region). New phenolic and carboxylic groups are formed from quinine radicals during photo-yellowing and in high-rich lignin pulps. Such groups could form strongly colored groups with metallic ions. Those factors cause degradation of optical properties, including brightness reversion. Peroxide can cleave the aliphatic lignin side chain if the C carbon has a carbonyl group ("Dankin reaction") (Andrady and Searle 1995).

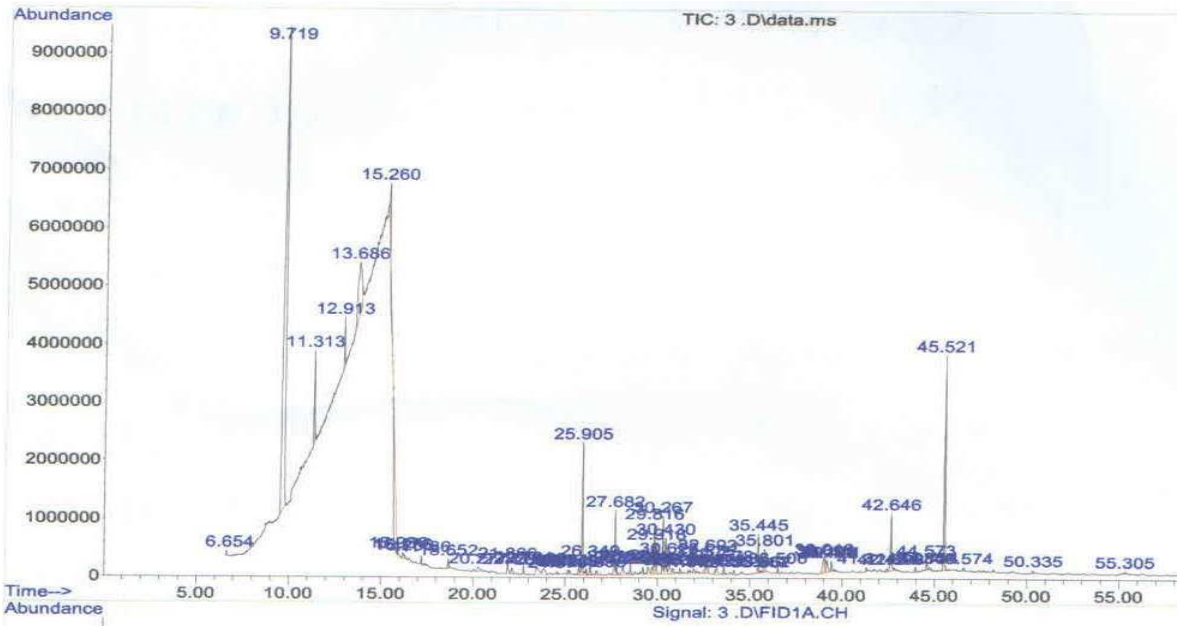

Fig. 1. Gas Chromatogram in samples of CMP pulps after bleaching.

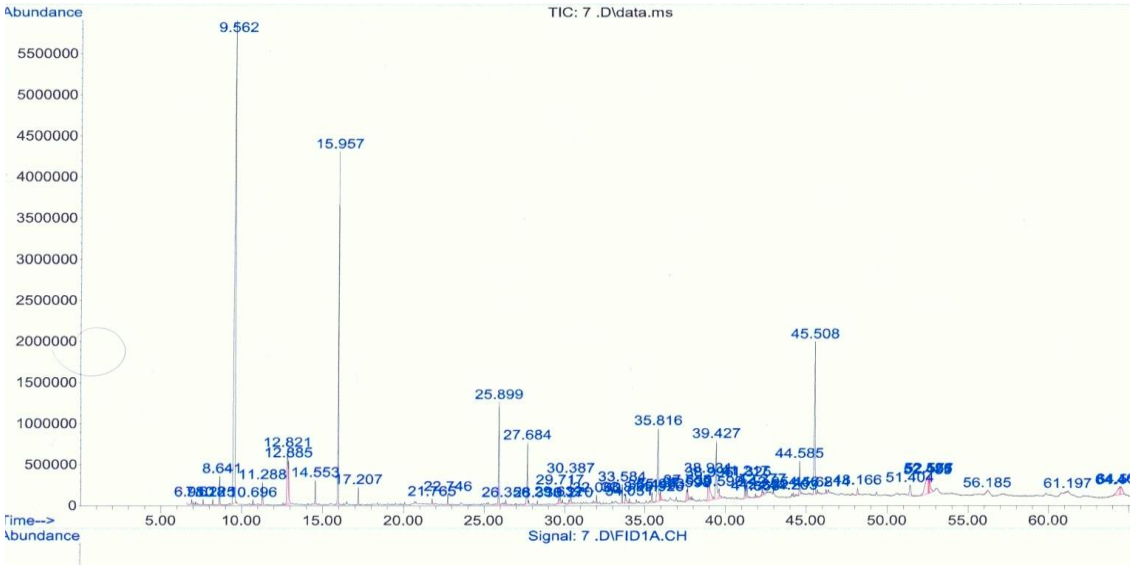

Fig. 2. Gas chromatogram in samples of newsprint**.**

The exhaustive ethanol-toluene of the bark and heartwood of Juglans regia L afforded pale red-colored extractives 10 and 12 % yields, respectively. Detailed chemical evaluation of these extracts using GC/MS revealed the major components in the bark and heartwood extractives to be the 3,7-dioxa-2,8-disilanonane and 2,2,8,8-tetramethyl (25.17 %), while the major heartwood extractives constituent was benzoic acid, 3,4,5-tri(hydroxyl)/gallic acid (44.57 %). The same components of the bark and the heartwood also contained amounts of the gallic acid, 3,7-dioxa-2,8-disilanonane, 2,2,8,8-tetramethyl, and d-glucose,2,3,4,5,6-pentakis-o-(hydroxyl). The most toxic components in the heartwood, were juglone (5.15 %) and 2,7-dimethylphenantheren (5.81 %) (Hosseini 2009).

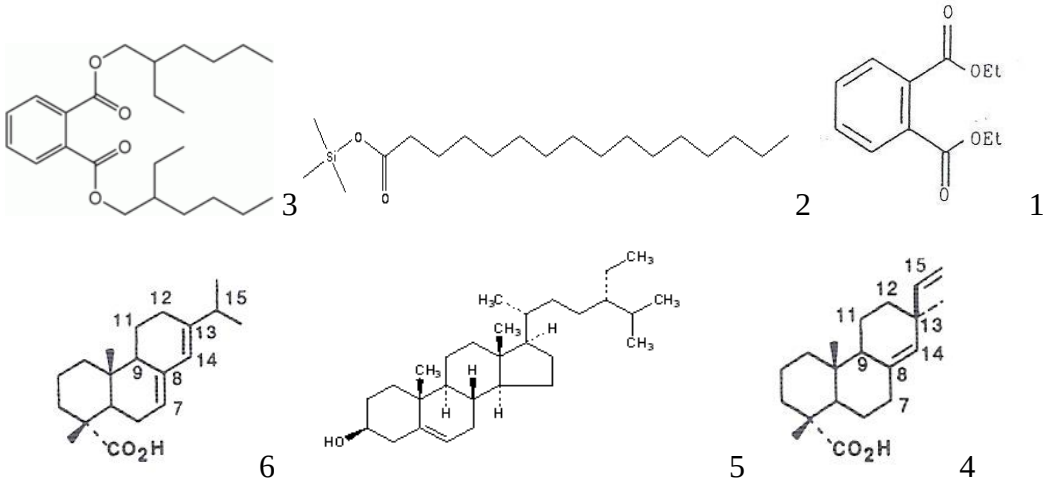

Fig. 3. Some of important components in CMP pulp and newsprint: 1,2-benzenedicarboxylic acid (1), hexadecanoic acid (2), bis (2-ethylhexyl) phthalate (3), pimaric acid (4), gamma-sitosterol (5), abietic acid (6)

This phenomenon has been attributed to a light-induced oxidation of the lignin present in the pulp. Extensive and comprehensive research, performed during the last decade, has given not only new information about the photochemical reactions causing yellowing, but also information on potential photostabilizing methods. However, to date, no single approach has become technically or economically feasible to meet all needs of the paper industry (Forsskahl and Tylli 1993; Ek *et al*. 1992). The resulting hydroquinone also is oxidized, to a *p*-quinone, by the action of secondary radicals arising from peroxide decomposition.

These new groups could result in the formation of colored groups with metallic ions. These factors can result in yellowing and brightness reversion. The catalytic activity of Mn^{2+} and Mn^{3+} in hydrogen peroxide decomposition has been studied by using DTPA as the only stabilizer. It was found that addition of DTPA to a Mn^{2+} containing system is more effective than if it is added to a Mn^{3+} containing system. To decrease the catalytic of Mn^{3+}, sodium borohydride and DTPA under an acidic condition were considered to reduce Mn^{2+} to Mn^{3+}. The effect of pH on using DTPA to decrease Mn induced peroxide decomposition has been discussed (Qiu *et al.* 2003).

Table 1. Analysis of Important Organic Chemical Compounds in CMP Pulps and Newsprint by GC/MS.

NO.	Chemical Component(C.C.)	Retention time(min)	Chips (%)	After cooking (%)	After bleaching (%)	News-print (%)
1	Xylene	6.910	3.39	-	-	0.19
2	1,2-Dimethyl-banzene	7.001	-	2.37	-	-
3	2,4-Pentadienenitrile	9.472	-	22.78	-	-
4	Benzaldehyde	9.562	13.29	15.27	46.49	32.53
5	Decan	10.694	0.48	0.27	-	0.18
6	Benzenemethanol	12.823	4.75	0.12	-	2.97
7	Benzyl alcohol	13.444	-	1.8	-	-
8	Formylmorpholine	15.332	1.57	1.55	-	-
9	Hydrochloric acid	16.173	-	-	1.99	-
10	Dodecane	17.208	1.85	0.79	0.32	0.63
11	Butanedioic acid	18.651	-	-	0.4	-
12	Octadecan	20.786	1.32	0.85	-	-
13	Benzeneacetamide	21.866	-	-	0.68	-
14	2,6-dimethoxy phenol	22.008	-	1.56	0.47	-
15	Tetradecane	22.745	0.95	0.65	0.28	0.37
16	Bibenzyl	25.902	4.8	0.39	4.55	3.82
17	Propanoic acid	27.68	-	2.0	2.15	2.27
18	Dodecanoic acid	28.315	0.39	0.08	-	0.14
19	Stilbene	30.268		-	2.09	-
20	Benzene ethanol	30.385	0.96	-	1.85	1.37
21	1,2-Benzendicarboxylic acid	33.58	4.09	0.9	1.28	0.71
22	Didutyl phthalate	35.44	0.68	1.74	1.30	0.48
23	Hexandecane	35.819	0.78	0.39	-	4.59
24	Hexandecanoic acid	35.786	4.07	-	1.03	-
25	Eicosane	35.974	2.56	0.88	-	-
26	9,12-Octadecadienoic acid	38.93	5.24	1.64	-	1.28
27	Oleic acid	38.995	-	-	-	1.84
28	Octadecanoic acid	39.428	0.89	0.55	-	3.55
29	9-Octadecadienoic acid	42.649	-	-	6.68	-
30	1-Nonadecane	44.584	-	2.42	-	-
31	1-Octadecane	44.584	0.5	-	-	1.44
32	Bis (2-ethylhexyl) phthalate	45.5	1.48	2.32	8.79	6.98
33	Gamma-Sitosterol	52.5	0.36	1.42	-	4.84
34	Beta-Sitosterol	56.26	5.2	-	-	-

CONCLUSIONS

The following conclusions could be drawn from the results of the present study:

1. The GC-MS diagram showed that benzaldehyde (13.29%), xylene (3.39%), bibanzyl (4.8%), benzenemethanol (4.75%), gamma-sitosterol (5.2%), beta-sitosterol (0.36%), and bis(2-ethylhexyl)phthalate (1.48%) were the most abundant components in chips for CMP pulp production.
2. In generally, 90, 76, 68, and 58 compounds were identified in chips, CMP pulp after cooking, the same after bleaching, and in newsprint sheets, respectively.
3. The results of this study showed that benzaldehyde (15.27%), bis(2-ethylhexyl)phthalate (2.32%), gamma-sitosterol (2.61%), beta-sitosterol (4.63%), benzyl alcohol (1.8%), 9,12-octadecanoic acid (1.54%), dodecane (1.58%), and 1,2-benzendicarboxylic acid (4.09%) were the most important components in CMP pulp after cooking.
4. In CMP pulp after cooking it was found that benzaldehyde (45.71%), hydrochloric acid (1.99%), bibanzyl (4.55%), propanoic acid (2.15%), bis(2-ethylhexyl)phthalate (8.79%), 9-octadecanoic acid (6.68%), bibanzyl (4.55%), and 1,2-benzendicarboxylic acid (1.28%) were the most chemical components.
5. In newsprint paper, benzaldehyde (32.56%), bis(2-ethylhexyl) phthalate (6.98%), gamma-sitosterol (4.84%) were the most abundant compounds, and the dodecanoic acid (0.14%), decane (0.18%), and xylene (0.19%) were the lowest detectable compounds respectively. Some compounds are very important in yellowing and brightness stability of newsprint.
6. The results of this study showed that benzaldehyde, dodecane, bibanzyl, 1,2-benzendicarboxylic acid, didutyl phthalate, and bis(2-ethylhexyl)phthalate were common chemical components in all of the samples.
7. Some extractives compounds have been proposed or considered as initiators or the main cause of yellowing in high-yield and mechanical pulps. Newsprint from bleached or unbleached CMP pulps are susceptible to photo-oxidative reactions, which cause the pulps to become discolored and to undergo brightness reversion. Identification of organic compound have been proposed or considered as initiators or the main cause of yellowing in high-yield and mechanical pulps.

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