

GC-MS ANALYSIS OF STICKY CONTAMINANTS IN A DEINKING PULPING LINE

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Pulps were sampled from three major points of a deinking pulping line and classified as fibers fraction, fines fraction, and aqueous phase, respectively, then extracted with tetrahydrofuran (THF) or methyl tert-butyl ether (MTBE). Sticky contaminants in the extractives were examined by GC-MS analysis. The results showed that the contaminants can be grouped as adhesive substances, wood extractives, lignin-derivatives, and other organic acids, of which the adhesive substances were accounted as the major component. Contents of sticky components in each group and their removal were further evaluated according to the related unit operation. Adhesives remaining in fibers and fines fractions were removed by the post-flotation. Wood extractives and degraded residual lignins were also released to some extent from pulp fibers during heat-dispersing, and then removed during the post-flotation.

Keywords: GC-MS analysis; Sticky substances; Deinked pulp; Fibers fraction; Fines fraction; Aqueous phase

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INTRODUCTION

Sticky contaminants continue to be a major problem in papermaking with deinked pulps. Such contaminants originate from ink-binding adhesives, coating adhesives, hot-melt adhesives, and pressure-sensitive adhesives from recovered papers, as well as lipophilic wood components released during the repulping processes (Hamann and Strauss 2002; Hubbe *et al.* 2006). They are usually identified as macro-stickies or micro-stickies, depending on their particle sizes, and primary stickies or secondary stickies, based on their origins. The term macro-stickies refers to tacky particles that are retained on a laboratory screen plate with slots of 100 μm or 150 μm , such that they often can be effectively removed through fine screening and cleaning processes in the deinking production line. Stickies smaller than 100 μm or 150 μm but larger than 1 to 5 μm have been called micro-stickies (Blanco *et al.* 2002; Doshi *et al.* 2003). The flotation process is an effective step for removal of both ink particulates and micro-stickies. Primary stickies result from the disintegration of adhesives and dissolution of wood extractives during pulping and subsequent stock preparation sequences. Secondary stickies come mainly from soluble and hydro-dispersible substances released during deinking pulping processes and exist in the form of dissolved and colloidal substances. They may be converted to sticky substances when the pH and temperature are changed and chemicals are introduced in the system (Hamann 2005; Li and Zhan 2005). These contaminants may

form troublesome deposits on the forming wire, press section, dryer section, and even on the surface of produced paper, deteriorating the paper machine runnability and negatively influencing paper product quality (Wells *et al.* 2007; Dechandt *et al.* 2004).

Stickies removal efficiency of major process units has been evaluated for a deinking line employing 100% recovered paper as raw material, and the results showed that the most efficient units for removal of stickies were the pre-flotation and the second thickening stage (Miranda *et al.* 2006). Different types of stickies demonstrated different attributes; macro-stickies can be used to monitor the removal efficiency of the process units, while micro-stickies predict calcium-soap deposits, and secondary stickies show the destabilization of the dissolved and colloidal substances. Therefore, an integrated approach is necessary for the full characterization of stickies throughout the papermaking process (Blanco *et al.* 2007). Studies by SEM-EDX and FTIR indicate that polyvinyl acetate, polyacrylates, styrene butadiene rubber, and derivatives of fatty acids and resin acids are the major stickies-related components identified in the deposits sampled from different units. Further investigation has revealed that some compounds are not selectively removed in the processes due to their recalcitrant nature (Carreño *et al.* 2008).

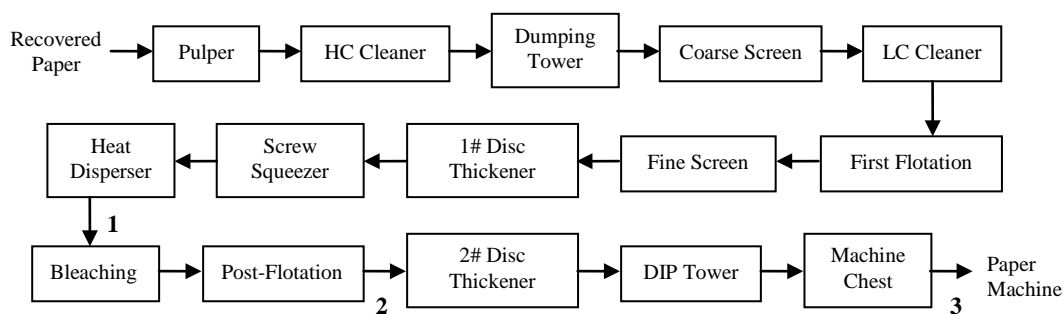
To reduce the obstacles caused by sticky contaminants, it is necessary to investigate compositions of sticky substances and further determine their behaviors in pulp suspension, so that appropriate approaches can be selected for effective control of them. The objective of this study was to identify and quantify different types of compounds in the sticky contaminants present in fibers, fines, and in the aqueous phase, to acquire better understanding of their behaviors in the papermaking process. Samples were taken from three major points of a deinking pulping line. Then they were classified as the fibers fraction, fines fraction, and aqueous phase, respectively. Furthermore, sticky substances in each fraction were examined by GC-MS analysis, and their removals were also considered according to the related process units in the production line. It is hoped that the preliminary results obtained from this investigation will provide some basic information for control of stickies in production of newsprint using deinked pulps.

EXPERIMENTAL

Pulp Samples and Their Fractions

As shown in Fig. 1, the pulp samples were taken from three major points in a commercial newsprint production line using 100% recycled fibers. The sample points were after the heat disperser, the post-flotation, and the machine chest, respectively.

Pulp sample, 10 grams (o.d.), was diluted with deionized water to 1% consistency and stirred at 60 °C for 1 hour. The fibers fraction was separated with a Dynamic Drainage Jar (DDJ, 200-mesh wire), as shown in Fig. 2. The filtrate was then centrifuged at 450 g for 20 min. to obtain the supernatant solution, which contained the dissolved and colloidal substances (DCS). The sediments remaining at the bottom of the centrifuge tube were considered the fines fraction (MacNeil *et al.* 2006; Sarja *et al.* 2006).



Sampling Point: 1. Heat Dispersing, 2. Post-Flotation, 3. Machine Chest

Fig. 1. Sampling points in the deinking pulping line

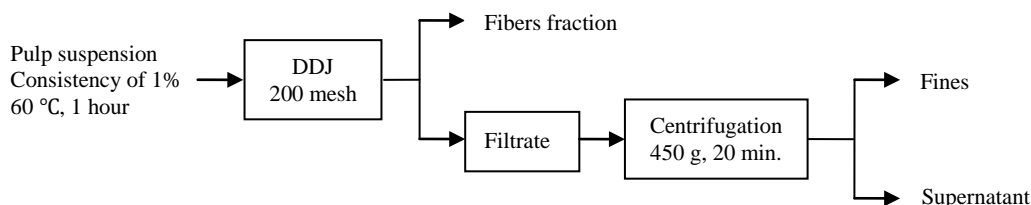


Fig. 2. Process of sample preparation

Extraction and Silylation of Fibers and Fines Fractions

The fibers and fines fractions were freeze-dried, then refluxed with 100 mL of tetrahydrofuran (THF) for 1 hour in a 250 mL round-bottom flask, filtered with a 0.22 μm membrane, and rinsed with 50 mL of THF. The solution was concentrated through evaporation, and further evaporated with a N_2 stream. The extractives were dried in a vacuum desiccator at 40 $^\circ\text{C}$ and weighed. Heneicosanoic acid, 0.04 mg, was added to the extractives as an internal standard, then the mixture was silylated with 25 μL of pyridine, 25 μL trimethyl-chlorosilane, and 80 μL of N,O-bis(trimethylsilyl)trifluoro-acetamide at 70 $^\circ\text{C}$ for 40 min. (MacNeil *et al.* 2006; Sarja *et al.* 2006; Voss and Rapsomatiotis 1985).

Extraction and Silylation of Aqueous Phases

The aqueous phase (2 mL) was placed into a screw-cap test tube, and one drop of bromocresol green was added as an indicator. Then the pH of solution was adjusted to about 3.5 by adding 0.25 M sulphuric acid, and the mixture was shaken until its color changed from blue to yellow. Next, 0.5 mL of methyl tert-butyl ether (MTBE) with 0.01 mg heneicosanoic acid was added into the solution as an internal standard. This was shaken for 3 min. to allow for a reaction, then centrifuged at 450 g for 5 min. The procedure was repeated twice, and the MTBE phase was collected. The obtained MTBE solution was evaporated in a N_2 stream, then dried in a vacuum desiccator at 40 $^\circ\text{C}$. The extractives were silylated with 25 μL pyridine, 25 μL trimethylchlorosilane, and 80 μL N,O-bis(trimethylsilyl) trifluoro-acetamide at 70 $^\circ\text{C}$ for 40 min. (MacNeil *et al.* 2006; Sarja *et al.* 2006; Voss and Rapsomatiotis 1985).

GC-MS Analysis

The GC-MS analyses were performed with a Shimadzu QP2010 Gas Chromatograph (Shimadzu, Japan), using a high temperature capillary column (DB-5, 30 m × 0.25 mm I.D., 0.1 mm film thickness), followed with an ion trap detector. The sample injection was 1.0 µL, and the diffluent ratio was 1:10. The temperatures of the injector and detector were 260 °C and 300 °C, respectively. The initial temperature of the column was 120 °C, and it was raised to 150 °C and held for 0.5 min. Next, there was a programmed raising of the temperature to 230 °C at a rate of 9 °C/min, and this was held for 5 min. Then the temperature was raised to 300°C at a rate of 10 °C/min and held for 1 min. Mass spectrum parameters were as follows: ion source temperature of 200 °C, interface temperature of 200 °C, and detector gain of 1.0 kV. Compounds in the analytes were identified by computer comparison of the mass spectra with those in the Wiley and NIST database.

RESULTS AND DISCUSSION

Pulp samples were classified as fibers fraction, fines fraction, and aqueous phases. Therefore, components examined in THF extractive or MTBE extractive samples represented, to some extent, macro-stickies, micro-stickies, and dissolved and colloidal substances in each fraction. Meanwhile their removal can be further discussed according to the related process units.

GC-MS Analysis of Extractives in Fibers Fraction

THF-extractives of fibers fractions were analyzed with a GC-MS, and the spectra of samples from three sampling points are shown in Fig. 3.

GC-MS analysis of THF-extractives showed that the organic components in fibers fractions came mainly from adhesive substances. They were composed of silicone oil, octadecamethyl-cyclonona-siloxane, eicosamethyl-nonasiloxane, silicone grease, and dibutyl phthalate. Fatty acids (hexadecanoic acid, *etc.*) and lignin-derivatives (phthalandione, *etc.*) were also identified in the extractives. Examined sticky substances in each sample could be grouped as adhesives, wood extractives, and lignin-derivatives, respectively. Their content and percentage based on their sampled points are listed in Table 1.

Table 1. Components in THF-Extractives of Fibers Fraction

Component	Heat Disperser		Post-Flotation		Machine Chest	
	(µg/g)	(%)	(µg/g)	(%)	(µg/g)	(%)
Adhesives	2608	96.1	2500	89.4	2695	85.5
Wood extractives	-	-	132	4.7	196	6.2
Lignin-derivatives	105	3.9	163	5.8	261	8.3
Total amount	2713	100	2795	100	3152	100

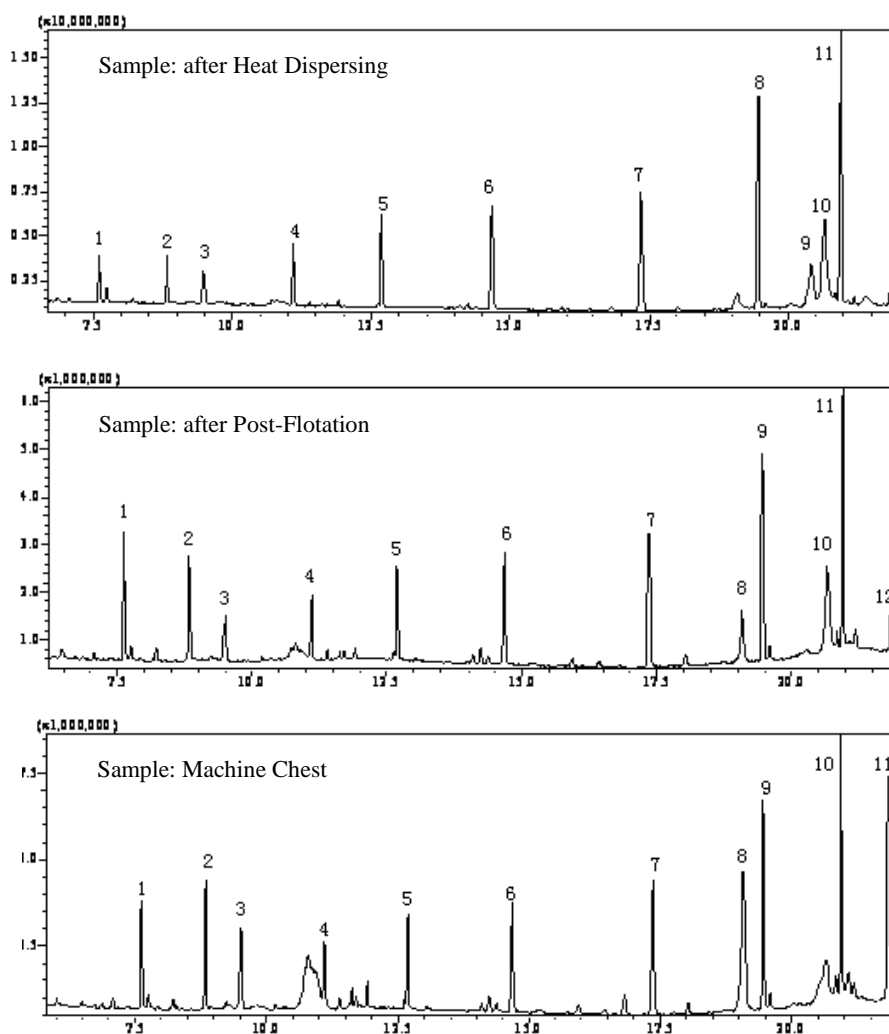


Fig. 3. GC-MS analysis spectra of THF extractives of fibers fractions

One can conclude from Table 1 that the adhesive substances were the major components in THF-extractives of the fibers fraction, accounting for *ca.* 96.1%, 89.4%, and 85.5%, respectively, for pulps sampled from the heat disperser, the post-flotation, and machine chest. Based on this investigation the content of adhesive components in fibers fractions decreased from 2608 $\mu\text{g/g}$ in the heat-disperser to 2500 $\mu\text{g/g}$ in the post-flotation, which means that about 4.1% of adhesive substances were removed through the post-flotation unit. It is understandable that after the heat dispersing step, macro-stickies remaining in the system can be effectively dispersed into micro-stickies, after which these micro-stickies were removed in the post-flotation. Combining with our previous study (Gao *et al.* 2012), removal of mini-stickies and micro-stickies were significantly enhanced in post-flotation after optimizing the operation of heat dispersing.

By contrast, adhesive substances increased to some extent in the machine chest. A possible explanation is that components remaining in the system may have agglomerated when the pH environment and temperature changed, as well as when

papermaking chemicals were introduced. Another reason could be the introduced process water, and especially white water in the system for pulp dilution may have increased the adhesive substances, though their amount was insignificant.

Wood extractives increased from a negligible amount in the sample from the heat disperser to 132 $\mu\text{g/g}$ in the post-flotation, while further to 196 $\mu\text{g/g}$ in the machine chest. Meanwhile, lignin-derivatives increased from 105 $\mu\text{g/g}$ in the sample from the heat disperser to 163 $\mu\text{g/g}$ in the post-flotation, and 261 $\mu\text{g/g}$ in the machine chest. This change can also be ascribed to the heat dispersion, which released wood extractives and degraded more residual lignins from the pulp fibers. Consequently, these components were attached on fibers and detected by GC-MS analysis.

GC-MS Analysis of Extractives in Fines Fraction

THF-extractives of fines fractions were analyzed by a GC-MS, and the spectrum of each sample are shown in Fig. 4.

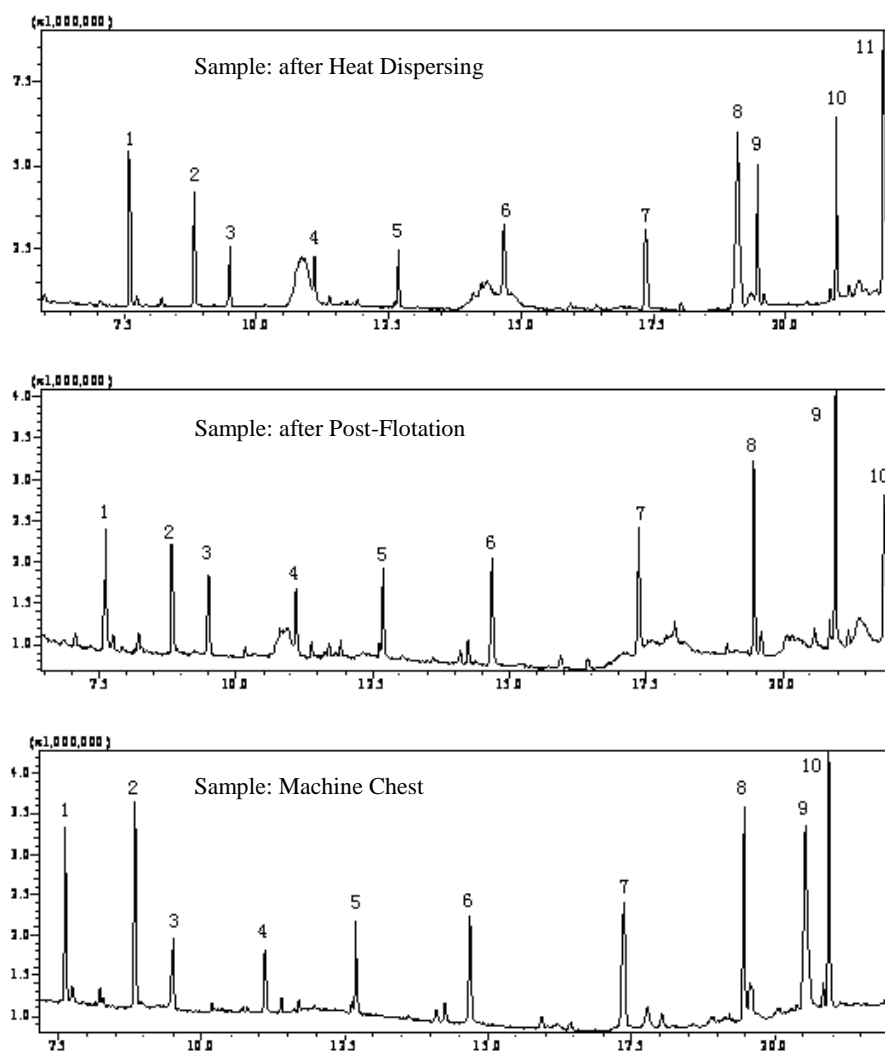


Fig. 4. GC-MS analysis spectra of THF extractives of fines fractions

Similarly, sticky substances identified in THF-extractives of fines fractions for each sample were mainly adhesive substances, including silicone oil, octadecamethyl-cyclononasiloxane, eicosamethyl-nonasiloxane, silicone grease, dibutyl phthalate, *etc.* Fatty acids (hexadecanoic acid, *etc.*), and lignin-derivatives (phthalandione) were also involved in identified substances. The results are listed in Table 2 according to their sampled points.

Table 2. Components in THF-Extractives of Fines Fraction

Component	Heat Disperser		Post-Flotation		Machine Chest	
	($\mu\text{g/g}$)	(%)	($\mu\text{g/g}$)	(%)	($\mu\text{g/g}$)	(%)
Adhesives	5190	81.7	3490	84.3	3570	84.4
Wood extractives	260	4.1	260	6.3	230	5.4
Lignin-derivatives	900	14.2	390	9.4	430	10.2
Total amount	6350	100	4140	100	4230	100

Obviously, the major components in THF-extractives of fines fraction were adhesive substances. They accounted for about 81.7% in the sample from the heat disperser, 84.3% in the post-flotation, and 84.4% in the machine chest, respectively. The post-flotation is a crucial process unit in a deinking system for removing markedly micro-stickies and dissolved and colloidal substances. In this investigation, about 32% of the adhesive substances in fines fractions were removed through the post-flotation, *i.e.* adhesive substances decreased from 5190 $\mu\text{g/g}$ (after heat-dispersing) to 3490 $\mu\text{g/g}$ (after post-flotation). It is easy to understand that the flotation effectively removes the particulates with sizes suitable for flotation. In fact, sizes of micro-stickies and colloidal substances are within this spectrum. Similarly, the content of lignin derivatives in fines fractions were also significantly decreased after flotation, *i.e.* from 900 $\mu\text{g/g}$ to 390 $\mu\text{g/g}$. Meanwhile, the amount of wood extractives changed slightly. It was noticed that the contaminants in the fines fractions did not show significant change from the post-flotation to the machine chest.

GC-MS Analysis of Extractives in Aqueous Phase

The MTBE-extractives of aqueous phases were analyzed by a GC-MS for each sample, and their spectra are shown in Fig. 5. Their contents and percentages are listed in Table 3 and compared based on the sampled process unit.

The sticky substances identified in aqueous phases of each sample were adhesive substances, including silicone oil, octadecamethyl-cyclononasiloxane, silicone grease, and dibutyl phthalate. In addition, other components were also examined in samples, including resin acids (dehydroabietic acid), fatty acids (hexadecanoic acid, octadecanoic acid), lignin-derivatives (phthalandione), and organic acids (pentanedioic acid, azelaic acid, benzoic acid, hexylic acid, hexenedioic acid, hexene diacid, glycine, lactic acid dimer, *etc.*).

It can be seen that the adhesive substances were still the major component in extractives of aqueous phases, which accounted for about 62.7% in the sample from the heat disperser, 77.1% in the post-flotation, and 70.7% in the machine chest. Compared to the total amount of 48.1 mg/L in the heat disperser, sticky substances in aqueous phases decreased to 42.9 mg/L after post-flotation, and further to 39.9 mg/L in the machine chest.

It was further confirmed that the sticky contaminants in the form of colloidal substances were to some extent removed by the flotation process.

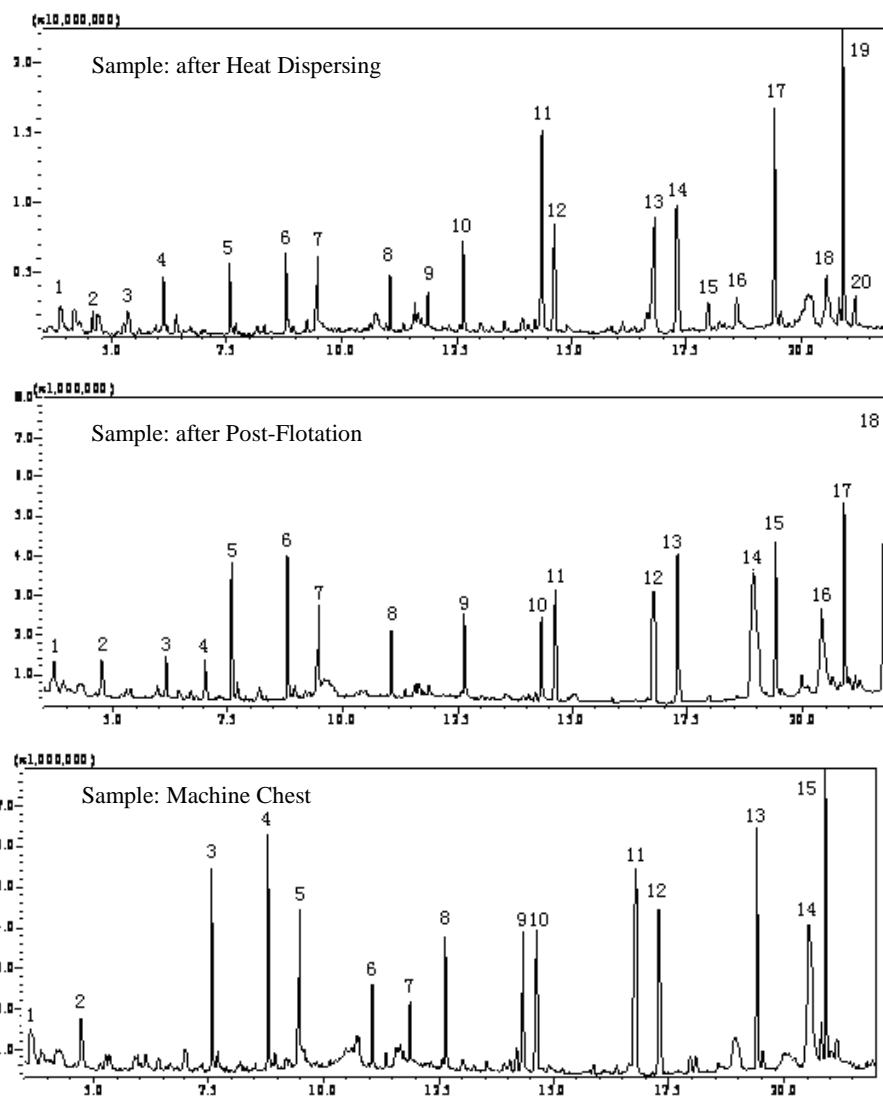


Fig. 5. GC-MS analysis spectra of MTBE-extracts of aqueous phases

Table 3. Components in MTBE-Extractives of Aqueous Phase

Component	Heat Disperser		Post-Flotation		Machine Chest	
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
Adhesives	30.1	62.7	33.1	77.1	28.2	70.7
Wood extractives	10.8	22.4	5.9	11.5	5.7	19.2
Lignin-derivatives	3.6	7.5	3.2	7.6	2.8	7.1
Other organic acids	3.5	7.4	1.7	3.8	1.2	3.0
Total amount	48.1	100	42.9	100	39.9	100

It is noticed that adhesive substances slightly increased from 30.1 mg/L in the sample in the heat disperser to 33.1 mg/L in the post-flotation. The post-flotation was performed under the pulp consistencies of 1.0 to 1.5%. Therefore, the probable reason for this increase was due to the process water and especially white water introduced into the system for pulp dilution, which brought in an extra amount of sticky substances and resulted in the slight increase of adhesive substances. Furthermore, it can be seen that the wood extractives decreased from 10.8 mg/L in the heat disperser to 5.9 mg/L in the post-flotation, and to 5.7 mg/L in the machine chest. Meanwhile, the lignin-derivatives decreased from 3.6 mg/L in the heat disperser to 3.2 mg/L in the post-flotation and 2.8 mg/L in the machine chest. Similarly, other organic acids decreased from 3.5 mg/L in the heat disperser to 1.7 mg/L in the post-flotation and to 1.2 mg/L in the machine chest, respectively.

CONCLUSIONS

1. Components of sticky substances identified in fibers fractions, fines fractions, and aqueous phases of deinked pulps can be grouped as adhesive substances, wood extractives, lignin-derivatives, and other organic acids. Among them, adhesive substances accounted as the major component.
2. Compared to the sample in the heat-dispersing, adhesive substances remaining in fibers fractions and especially in fines fractions were removed by the post-flotation. Similarly, the content of lignin derivatives in fines fractions were also significantly decreased after the post-flotation.
3. The adhesive substances were still the major component in extractives of aqueous phases, and their amount decreased after post-flotation. Wood extractives and lignin-derivatives were released to some extent from pulp fibers during heat-dispersing and then removed during the subsequent post-flotation.

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