

# Schlussbericht

## zum Vorhaben

Thema:

**Ersatz von BPA durch holzstämmige Verbindungen – "Grüner Entwickler"**

Zuwendungsempfänger:

**Universität Hamburg**

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## Schlussbericht

### I. Ziele

The overall goal of the project is to search for an alternative to Bisphenol A (BPA) “developer” for leuco dye systems based on renewable raw materials and to develop a new product. Such dye systems whose colour is induced by heat pulses are the most important functional component in thermal papers. The use of BPA as a developer in conventional thermal papers is critical to environmental and health hazards. This has called for a rigorous research to replace the petrochemical-based BPA with renewable resources to encourage “green development” in thermal paper and similar thermochromic systems.

The project was planned according to the project plan and workflow (**Figure 1**).

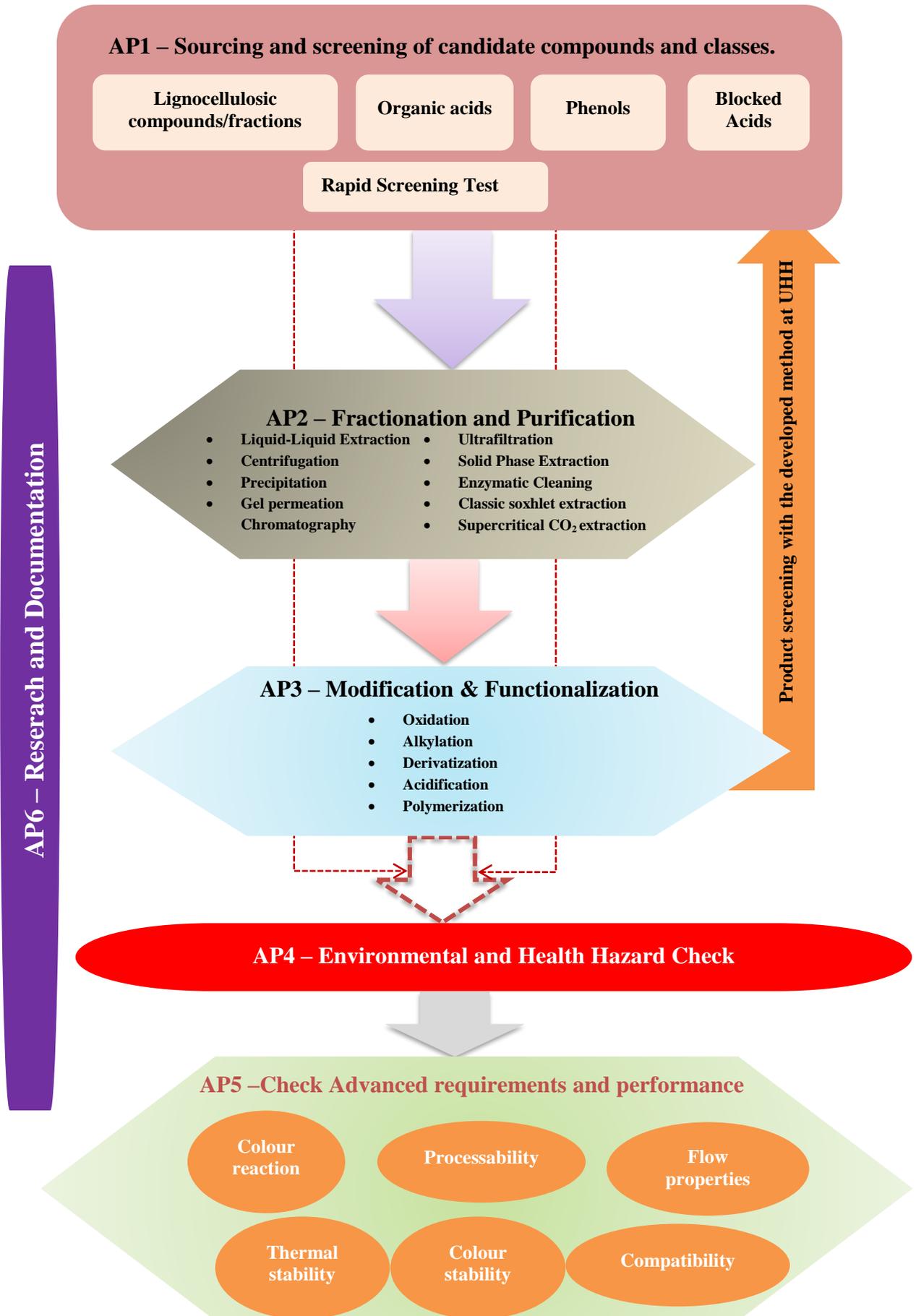


Fig 1. Proposed project plan and workflow

## 1. Aufgabenstellung

The target "green developer" is expected to fulfil the optimum requirement for the intended use as a developer in leuco dye systems in colour active layers of thermal papers. Requirements are:

- inducing the colour reaction by heat pulses at the specific temperature of application. This depends on the melting point
- acid-base properties; ability to transfer protons to a leuco dye.
- colour density, colour sensitivity and colour stability under different conditions
- a solid aggregate state at normal conditions.
- solubility, preferably not / slightly soluble in water.
- thermal stability.
- storage stability.
- inherent colour; preferably colourlessness so that there is no background imaging on application
- flow properties; compatibility and processability
- appropriate permanence for the application under different conditions
- low or no toxicity for health and environment
- appropriate performance vs cost balance
- feasible in large-scale production and low manufacturing costs

The project has been designed for a period of 24 months. After 12 months, evaluations of the results were made. During this period, many compounds and fractions from the target group were evaluated with the developed screening technique to assess their suitability in principle. Suitable compounds from the results of the characterization tests are thereafter extended (AP5). These results allow a first evaluation of the functionality and the economic burden connected with the production of "green developer" in order to decide on a meaningful continuation of the project. This review is carried out in the framework of a project meeting of project participants - **Universität Hamburg (UHH), Mitsubishi HiTec Paper Europe (MPE) and Fachagentur Nachwachsende Rohstoffe (FNR)**. Table 1 below describes the planned timing of the individual work packages and the milestones set within the project. The bars depicted in the schedule does not mean the man specific months in the work packages (MM) but indicate the period over which respective sub-task will be undertaken. "MS" as the imaginary "milestone" result meeting the project participant is also identified in the bar chart.

**Table 1: Time schedule of the individual work packages and milestones**

Work Packages	Months							
	1 - 3	4 - 6	7 - 9	10 - 12	13 - 15	16 - 18	19 - 21	22-24
AP1: Sample procurement and Screening								
AP2: Fractionation and Cleaning								
AP3: Modification								
AP4: U & G vulnerability								
AP5: ext. Conditions								
AP6: Research and Documentation								

## 2. Stand der Technik

The following chapter describes the state of the art in science and technology of the technical work packages (AP 1 to AP 5) on which the collaborative project has been based.

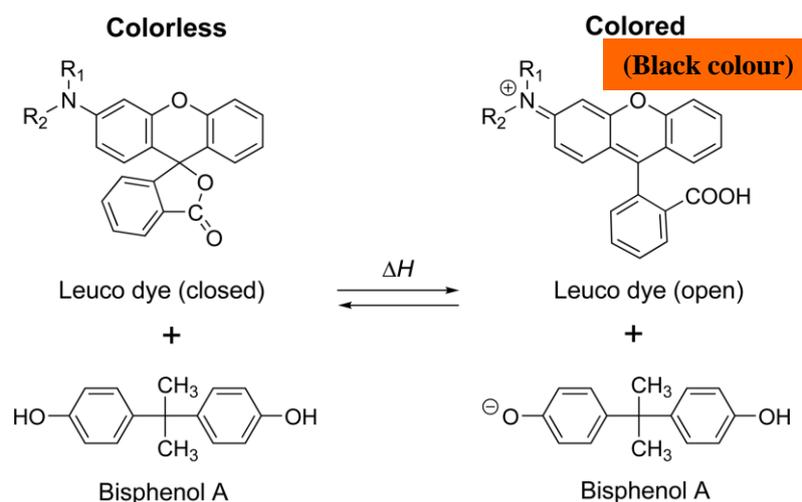
### AP1 Sourcing and screening of candidate compounds and classes

Lignocellulosic based compounds and fractions, in pure form, were sourced and tested for their developing potentials using the rapid screening method developed in our laboratory (Huneke, 2014). This test serves as a preliminary investigation before the advanced requirements (AP5) are adequately studied.

In order to initiate the potential colour-developing capabilities of the compounds and fractions, preferred leuco dye from MPE, ODB-2 (one dye black = 2-Anilino-6-dibutylamino-3-methylfluoran) is used as the colour former. Colour reaction is premised on the mechanism of known colour reaction (Jang *et al.*, 2013) (**Figure 2**). The overriding quality of a developer is attributed to its ability to transfer protons to colourless leuco dyes thereby triggering colour formation. In this case, organic acids, blocked acids, phenols and substances having acid functionality are potential candidates (Yamaguchi, 1991). Materials screened are individual compounds and fractions from current or already completed projects, from existing collections or originated from industrial processes.

Examples include:

- Electrochemical modified lignin from a current ZIM project of TI.
- Bio-oils by fractional condensation from running project
- Organosolv lignin from ongoing projects
- Black liquor from private timber outcrops for pulp production
- Lignin fractions of hydrothermal treatment of straw - from current project
- Components from the institute's collection of lignins and other extractives
- Bark extracts – Sappi
- Commercially available extracts
- Extracts obtained from extractions of various tree species and tissue parts etc.



**Figure 2. Reversible colour-formation reaction between leuco dye and bisphenol A (BPA).**

In addition, previously established acetone test, FTIR analysis (Rihs and Weis 1991) and UV spectrometry analyses (Hojo *et al.*, 2009) were further carried to ascertain the interaction the screened compounds and the leuco dye.

## AP2 Fractionation and Purification

Fractionation is carried out to simplify the mixtures making it easier to characterize, determine the exact functionality responsible for colour formation and also allowing for easier environmental and health impact assessment. Several fractionation and purification methods are considered and detailed in subsequent chapters.

### AP2.1 Fractionation of pulping liquor

Fractionation of valuable chemicals from lignocellulosic biomass is currently an area of significant research interest. This is occasioned by the urgent need to provide viable alternatives to fossil-based resources, which have hitherto being the mainstay of man's sustenance albeit now considered to pose proven health and environmental challenges (Thompson *et al.*, 2009). The delignification of wood biomass to produce pulp termed 'pulping' is an important step in the production of paper and paper products. Kraft pulping, which involves the use of NaOH and Na<sub>2</sub>S as the primary pulping chemicals, is the most widely used process for the delignification of wood owing to the high quality of resultant pulp (Cardoso *et al.*, 2009). During this process, wood components such as lignin and

carbohydrates are degraded, and their degradation products dissolved in the pulping liquor resulting in a waste stream called black liquor. Regardless of the pulping process used, the type and source of wood biomass processed, black liquor is usually a complex mixture of valuable organic and inorganic compounds, which can be isolated and processed into value-added bio-products (Niemi *et al.*, 2011). Although isolation of individual components of black liquor remains a challenge, several process technologies have already been investigated and established to fractionate high molecular weight lignin and various classes of compounds (Kumar and Alen, 2015).

The aim of this work package is to separate the high molecular weight compounds from the low molecular weight compounds and further purify the low molecular weight compounds into individual compounds or less complex fraction. The colour developing potential of the compounds and fractions is then tested with our screening method (AP1) after characterization.

In addition, tannin extracts are complex mixtures of phenolic substances, sugars, organic acids and carbohydrates (Missio *et al.*, 2017). Purification of industrial tannin samples is therefore imperative for extended applications

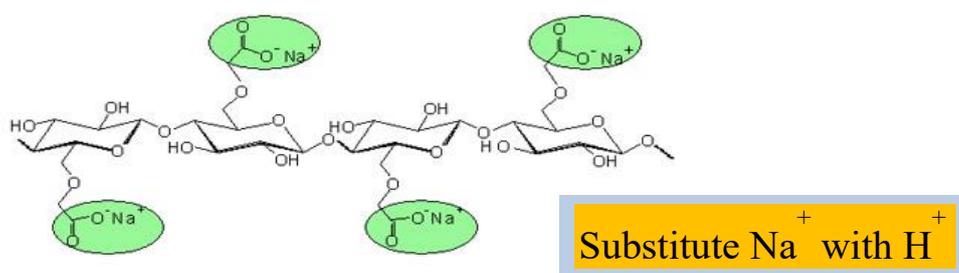
The following summarises some the tasks under this work package (2.1)

- *Isolation/Precipitation of high molecular weight lignin*
- *Liquid-Liquid Extraction of filtrate*
- *Fractional Vacuum Distillation of Extracts*
- *Characterization of distillate*
- *Screening of distillates*
- *Further fractionation of extracts:- Acid-base fractionation of extract; solid phase extraction of extract; gel permeation chromatography (GPC)*
- *Screening of GPC Fractions*
- *Ultrafiltration of Kraft black liquor*
- *Sequential fractionation of lignin*
- *Soxhlet extraction of Tannin*

## AP3 Modification

### AP3.1 Acid hydrolysis of carboxymethylcellulose (Na-CMC)

Na-CMC, a sodium salt of Carboxymethylcellulose (CMC) (Figure 3), is produced by substituting carboxymethyl groups for some of the hydrogens of hydroxyl groups present in each anhydroglucose unit of cellulose. Properties of Na-CMC produced depend on carboxymethyl groups substituted per monomer unit. It is considered health and environmental friendly with its high molecular weight limiting its ability to penetrate into the skin. Na-CMC is an anionic polyelectrolyte which dissociates into a multivalent polyion and a large number of counterions of opposite charge in aqueous medium due to the presence of weakly acidic groups (Carlos *et al.*, 2015). The release of these active groups makes Na-CMC susceptible to different modifications and as such makes it useful in wide variety of applications such as thickeners, emulsifiers, conditioners, clarifying agents, in water treatment, food, cosmetics and pharmaceutical products.



**Figure 3.** Structure of Sodium Carboxymethylcellulose

### AP3.2 Derivatization of extracts

Derivatization is the process of chemically modifying a compound to a new product with same chemical structure called derivative that are suitable for the analysis using GC or HPLC. The main aim of this method is to modify the functional groups of the reacting compound so that it can be easily detectable and systematically analyzed. Common derivatization methods include Silylation, alkylation, acylation and chiral derivatization. Silylation is used in the conversion of a compound to its trimethylsilyl derivative. Alkylation works by replacing the active hydrogen with alkyl groups to produce esters, ethers, alkylamides and alkylamines. Acylation also reduces the polarity of the reactive functional groups such as amino, hydroxyl and thiol groups (Salimon *et al.*, 2014).

### AP3.3 Oxidation

Oxidation is a well-established technique in industrial chemical processes. This method involves the oxidation of a reactant and subsequent isolation of the oxidized product using an organic solvent (Kiely 2000)

### AP3.4 Bulk Polycondensation

Solvent-free bulk polycondensation of multifunctional molecules have been reported (Sivasankarapillai *et al.*, 2012, Izabela *et al.*, 2013, Santiago-Medina *et al.*, 2017). This process is aimed at the exploitation of the multifunctional properties of bio-based molecules for the production of high value polymers.

### AP3.5 Esterification of Tannin

Tannins are renewable and plant-based polyphenolic compounds with huge potential for valorization. Esterification of Tannin is done to introduce new functional groups such as acyl group to Tannin (Grigsby *et al.*, 2013).

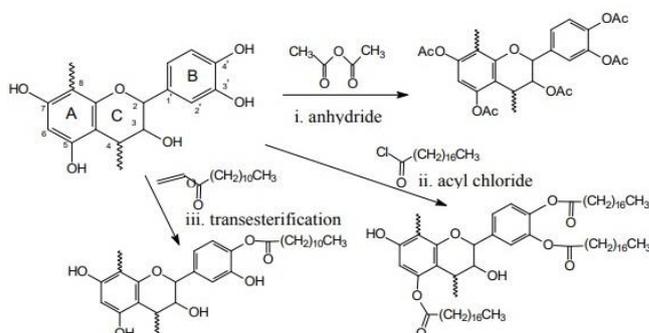


Figure 4. Reaction scheme showing various routes to tannin ester formation (Grigsby *et al.*, 2013)

### AP3.6 Tannin modification with Metal ion

Alkali metals, alkaline earth metals and transition metals (Mg, Ca, Li, Na, Zn etc.) have been reported to have the ability to open the lactone ring of a leuco dye and also produce colour in

a non-aqueous environment (Hojo 2009 & 2012). Metal-modified resin developer has also been reported (Saito 1976; Yamaguchi, 1991; Yamaguchi, 1994; Kornherr 2012).

### **AP3.7 Amination of Tannin and biobased phenolics**

Phenol-amine complex are potential developers in thermal recordings (Lawton, 1978). Since Tannins and polyphenolic compounds, they can be used as source of phenols for the formation of phenol-amine complex.

### **AP5 Check advanced requirements and performance**

The performance characteristics and evaluation of pure compounds, fractionated compounds, purified and modified compounds were carried out by our industrial partner Mitsubishi HiTec Paper Europe (MPE). Evaluation process includes the preliminary dry and wet testing of the compounds and the production of coating dispersions for subsequent application on pre-coat papers. Characteristic of image formed such as optical density and stability under heat and moisture was also done using industrial hardware.

### **Literature on the state of the art in science and technology**

Huneke, A. Development and application of a test method for testing alternative developers in thermal paper. Seminar work. University of Hamburg. Centre for wood research. 2014

Jang, Y. I; Choi, W.-H; An, B.-K. (2013): Hyperbranched poly (aryl ester)s as Developers Materials for Thermal Printing System. In: *Bulletin of the Korean Chemical Society* 34 (4), S. 1225-1231

Yamaguchi, K. (1991). Salicylic acid copolymers and their metal salts, production process thereof, colour producing agents comprising metal salts of the copolymers and colour developing sheets employing the agents. US Pat. No. 5,023,366

Hojo, M; Ueda, T; Inoue, A; Tokita, S. Interaction of a practical fluoran-based black color former with possible color developers, various acids and magnesium ions, in acetonitrile. *Journal of Molecular Liquids* 148 (2009) 109–113

R.C. Thompson, C.J. Moore, F.S. vom Saal, S.H. Swan, *Plastics, the environment and*

human health: current consensus and future trends, *Philos Trans R Soc Lond B Biol Sci*, 364 (2009) 2153-2166.

M. Cardoso, É.D. de Oliveira, M.L. Passos, Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills, *Fuel*, 88 (2009) 756-763.

H. Kumar, R. Alén, Recovery of aliphatic low-molecular-mass carboxylic acids from hardwood kraft black liquor, *Separation and Purification Technology*, 142 (2015) 293-298.

H. Niemi, J. Lahti, H. Hatakka, S. Kärki, S. Rovio, M. Kallioinen, M. Mänttari, M. Louhi-Kultanen, Fractionation of Organic and Inorganic Compounds from Black Liquor by Combining Membrane

Francisco-Jose Santiago-Medina, Antonio Pizzi, Maria Cecilia Basso, Luc Delmotte and Alain Celzard (2017). Polycondensation Resins by Flavonoid Tannins Reaction with Amines. *Polymers*, 9(2), 37

Gopakumar Sivasankarapillai, Armando G. McDonald, Hui Li (2012). Lignin valorization by forming toughened lignin-co-polymers: Development of hyperbranched prepolymers for cross-linking. *bio mass and bio energy* 47 99e1 0 8

Taubner T, Synytsya A, Čopíková J (2015). *Int J Biol Macromol*. Jan;72:11-8. doi: 10.1016/j.ijbiomac.2014.07.049. Epub 2014 Aug 9. Preparation of amidated derivatives of carboxymethylcellulose.

Sanna Hellstén, Jussi Lahti, Jari Heinonen, Mari Kallioinen, Mika Mänttari, Tuomo Sainio (2013). Purification process for recovering hydroxy acids from sodablack liquor. *chemical engineering research and design* 91 ( 2 0 1 3 ) 2765–2774

### **3. Zusammenarbeit mit anderen Stellen**

This project was technically done in conjunction with Mitsubishi HiTec Paper Europe (MPE). The first line screening of all compounds and materials including fractionation, purification and modifications were done at the University of Hamburg. MPE was essentially on hand to carry out the extended testing of all the materials as aforementioned.

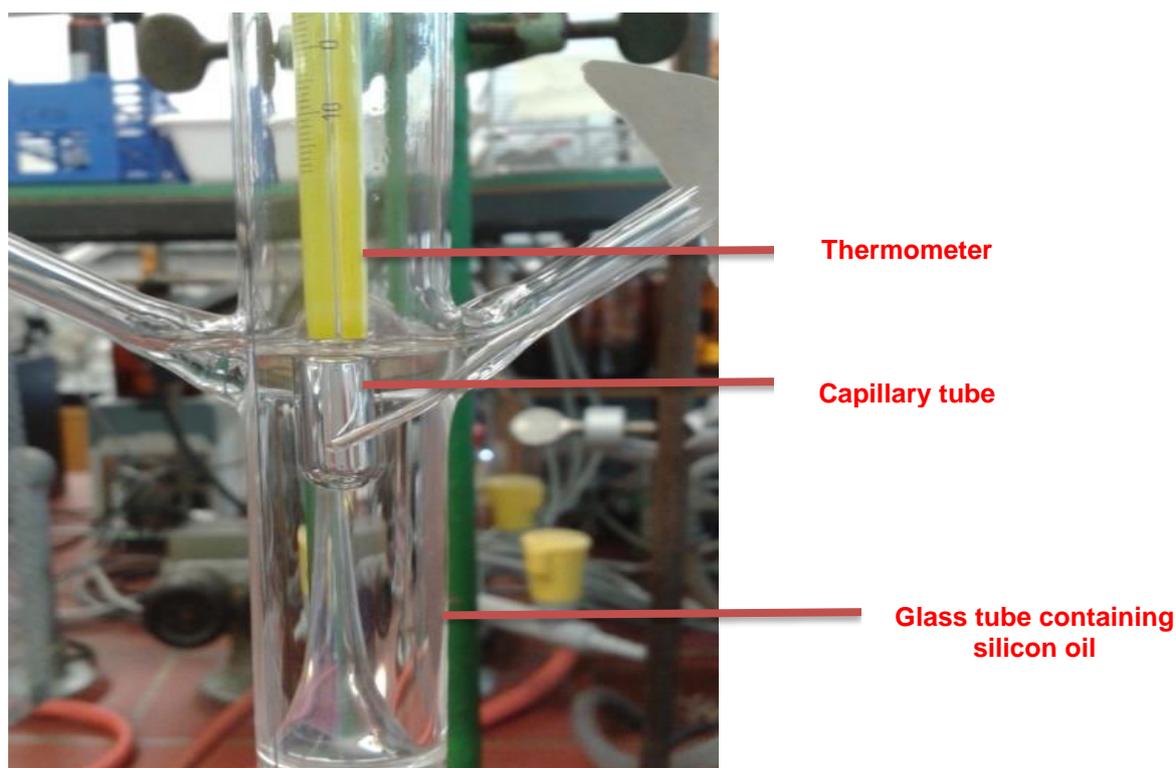
## II. Ergebnisse

### 1. Erzielte Ergebnisse

#### AP1 Sourcing and screening of candidate compounds and classes

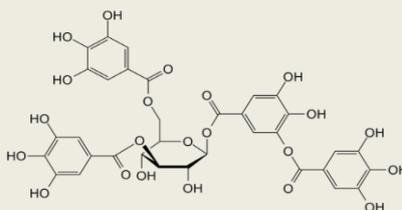
##### AP1.1 Screening of lignocellulosic compounds

In the screening method (**Figure 5**), pulverized mixture of known weight sample and leuco dye was filled into a capillary tube of 80 x 1.5mm to a height of about 3 mm. This was done by immersing the open side of the tube in the substance and then tapping the bottom of the tubes on the bench to allow for settling of the sample in the tube. The capillary tube, tied to a thermometer, was dipped into the silicone oil through a clamped cork. The oil was heated with a bunsen burner and colour change was observed as temperature changes. Two parameters were simultaneously observed – the colour change and temperature at which the change occurs. The temperature of melting – if any- was also determined. Overall about 50 compounds and fractions across 14 classes were screened. The results of individual tests are highlighted in table 2 and compared with the results observed with the commonly used developer – BPA mixture. Images presented were captured with a digital microscope VHX-500FD Keyence equipped with zoom lens VH-Z20R with 20- to 200-fold magnification.



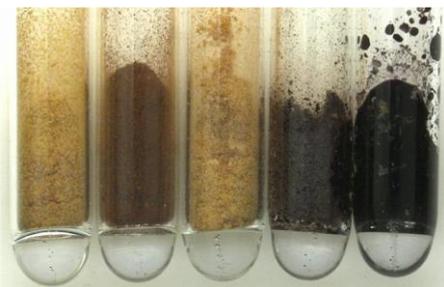
**Fig. 5: Screening process set-up**

## TANNINS



Tannins are highly abundant source of natural biomolecules found in various vascular plants. They are very good building blocks to develop polymers and materials due to their multifunctionality brought by phenolic and aliphatic hydroxyl groups. Tannins are divided into two different classes: hydrolyzable tannins (HT) and condensed tannins. This study investigates Tannins samples from the two classes.

### Catechu



**Left to right:**

(1) Catechu (\*UH),

(2) Catechu (\*\*H),

(3) Catechu : ODB-2 (UH),

(4) Catechu : ODB-2 (H),

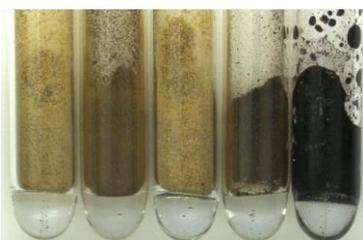
(5) \*\*\*BPA : ODB-2\*\*\*\* (H).

**\*UH = Unheated; \*\*H = Heated; \*\*\*BPA = Bisphenol A; \*\*\*\*ODB = one day black = 2-Anilino6-dibutylamino-3-methylfluoran**

**\*\*\*This will be repeated all through the report\*\*\***

The powdery tanning agent catechu has a light brown colour. When heated, it turns dark brown as the temperature rises. A reason for the darkening could be a result of thermal degradation but this is uncertain. The mixture of the colourant ODB-2 and Catechu has a beige colour. When heated, the mixture gives an obvious black colouration. The black colouration first appears at a temperature of 175 °C and then turns dark brown and finally to stable black at 230 °C. Although, the observed colour is not completely similar to the colour from the reference but it suggests that a possible reaction might have occurred between catechu and the colourants. This makes Catechu a promising candidate as developer.

## Technical Tannin



### *Left to Right:*

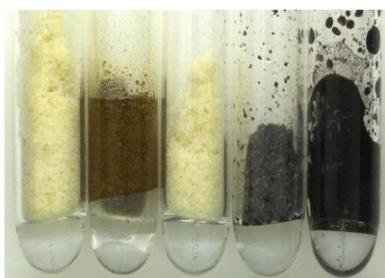
(1) Tannin (technical) (**UH**), (2) Tannin (technical) (**H**),

(3) Tannin (technical):ODB-2 (**UH**),

(4) Tannin (technical):ODB-2 (**H**), (5) BPA:ODB-2 (**H**).

brown when slightly heated but remains unchanged with the addition of the colourant. The mixture however turns darker at a temperature of 180 °C and remains dark brown at 230 °C. In comparison with the colour result of the reference, it becomes clear that the technical tannin does not lead to the expected black colouring and could possibly not function as a developer.

## Pure Tannin



### *Left to Right:*

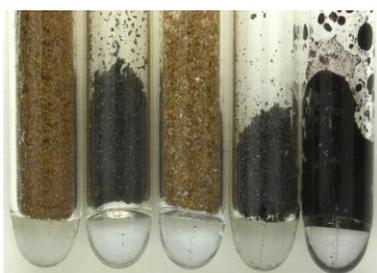
(1) Tannin (Pure) (**UH**), (2) Tannin (Pure) (**H**),

(3) Tannin (Pure):ODB-2 (**UH**),

(4) Tannin (Pure):ODB-2 (**H**), (5) BPA:ODB-2 (**H**).

Pure tannin has a light beige-white colour. When heated using the rapid test apparatus, it turns medium brown at a temperature of about 180°C - 200 °C. The mixture of pure tannin and colouring agent also has a light colour, which changes to black-grey when heated. The mixture turns grey at 150 °C and black when the colourant melts at 179 °C. In comparison with the reference, the pure tannin functions as a developer in principle. The colouring is less intense but the colour difference between the unheated pure tannin and the heated mixture is clear.

## Chestnut extract



### *Left to Right:*

(1) Chestnut Extract (**UH**), (2) Chestnut extract (**H**),

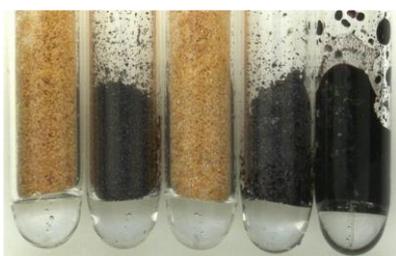
(3) Chestnut extract:ODB-2 (**UH**),

(4) Chestnut extract:ODB-2 (**H**),

(5) BPA:ODB-2 (**H**).

The untreated chestnut wood extract is brownish in appearance. Under the influence of heat, it turns black between 180°C and 230 °C. The mixture of colouring agent with chestnut wood extract is medium brown and turns black when heated to a temperature of 190°C. The black colour remains unchanged at 225 °C. The colour result is comparable to the reference. Chestnut wood extract contains flavonoids, which could possibly react with colouring agent to produce the expected black colour. Notable limitation is the black colour produced by chestnut extract without the addition of the colouring agent. This colour maybe attributed to possible thermal oxidation or degradation. Moreover, the intrinsic colour of the chestnut extract is a disadvantage for industrial processing. However, the valuable component of the extract may be isolated and tested for its developer potential.

### Mimosa Extract



*Left to Right:*

- (1) Mimosa Extract (UH), (2) Mimosa Extract (H),  
 (3) Mimosa Extract:ODB-2 (UH),  
 (4) Mimosa extract:ODB-2 (H), (5) BPA:ODB-2 (H).

Mimosa extract is less strongly coloured than chestnut wood extract, but also has egg-like colour. Similar to the result obtained from chestnut extract, Mimosa extract also produces a black colouring on heating to 180°C. The black colour of the mixture of the extract and the colourant develops at 190°C and remains at 230 °C. Mimosa extract, like chestnut wood extract, in principle, functions as a developer.

### Quebracho Extract

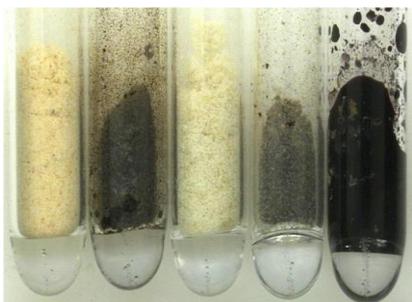


*Left to Right:*

- (1) Quebracho Extract (UH), (2) Quebracho Extract (H),  
 (3) Quebracho Extract:ODB-2 (UH),  
 (4). Quebracho extract:ODB-2 (H), (5) BPA:ODB-2 (H).

Quebracho extract is light brown. When heated, it turns reddish-brown. The beige-brown mixture of quebracho extract and colourant turns dark red-brown when exposed to heat. In comparison with the reference it is clear that the Quebracho extract does not work as a developer.

## Tara



### **Left to Right:**

(1) Tara (UH), (2) Tara (H),

(3) Tara:ODB-2 (UH),

(4) Tara:ODB-2 (H) , (5). BPA:ODB-2 (H).

Tara has a light beige/near white colour which changes to dark brown on heating between 120°C to 180 °C. The mixture of Tara and colourant is also light beige. The discolouration of the mixture begins at 120 °C and continues at 180 °C. In comparison with the reference, Tara works as a developer in principle. The difference between the untreated and the heated mixture is too obvious to be ignored. Worryingly, without the addition of the colourant, when heated, Tara only produced a dark colour which appears more intense than that of the heated mixture.

## OLIGOMERIC PROANTHOCYANIDINS

Proanthocyanidins are a class of polyphenols found in a variety of plants. Chemically, they are oligomeric flavonoids. Oligomeric proanthocyanidins (OPC) strictly refer to dimeric and trimeric forms of catechins. They are found in most plants and thus are common in the human diet. Especially, the skin, seeds, and seed coats of purple or red pigmented plants contain large amounts of OPCs. They are dense in grape seeds and skin, and therefore in red wine and grape seed extract, cocoa, nuts and all *Prunus* fruits (most concentrated in the skin). OPCs also can be found in blueberries and cranberries. (Carpenter *et al.*, 1994).

## Grape Seed Extract (GSE)



### **Left to Right:**

(1) GSE (UH),

(2) GSE (H),

(3). GSE:ODB-2 (UH),

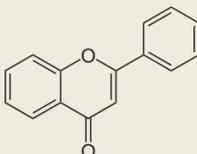
(4). GSE:ODB-2 (H),

(5). BPA:ODB-2 (H).

The light brown grape seed extract turns red-orange on heating to 100 °C. With the

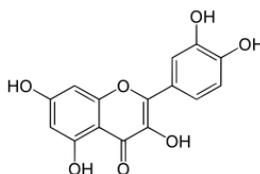
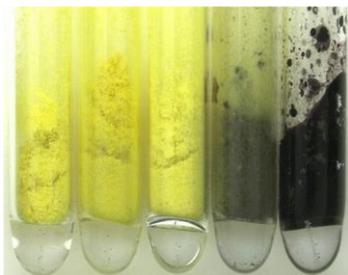
addition of the colourant, a black colouration was produced when heated. This colour formation begins gradually at 130°C and remains unchanged at 230 °C. The heated mixture is coloured black, but small red spots are visible. This may be due to the fact that the potential developer has not been fully implemented. A higher combination ratio of the developer and colourant may remove the unwanted red spots.

## FLAVONOID



Flavonoids are the largest group of phytonutrients responsible for various health benefits associated with diets rich in fruits and vegetables. Onions, tea, strawberries, kale, grapes, citrus fruits and many others natural foods are rich in flavonoids.

## Quercetin

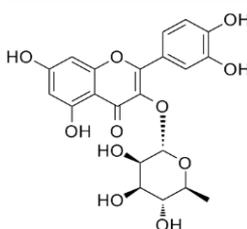
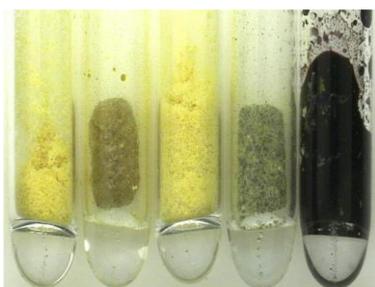


### Left to Right:

- (1) Quercetin (UH), (2) Quercetin (H),
- (3) Quercetin:ODB-2 (UH),
- (4) Quercetin:ODB-2 (H),
- (5). BPA:ODB-2 (H).

Quercetin is a yellow, powdery substance. The melting point could not be determined in the temperature range used for the screening. The light yellow mixture of quercetin and colourant slowly turns grey at a temperature of 180°C and black at 230 °C. In principle, Quercetin seems to work as a developer. The intrinsic deep yellow of the sample might be a cause for concern.

## Quercitrin

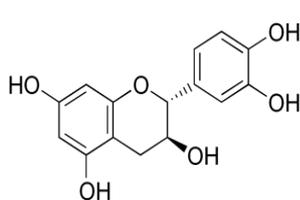


### Left to Right:

- (1). Quercitrin (UH),
- (2). Quercitrin (H),
- (3). Quercitrin:ODB-2 (UH),
- (4) Quercitrin:ODB-2 (H)
- (5). BPA:ODB-2 (H).

The results of the rapid test of Quercitrin are similar to those of Quercetin. Quercitrin is also a yellow, powdery substance that melts at a temperature of 172 °C and turns medium brown on heating. The yellow mixture of Quercitrin and colourant turns grey-black at 158 °C. Quercitrin seems to function as a developer in principle. Though the black is not fully developed but it suggests an ensuing reaction.

### Insoluble Catechin (ICat)



**Left to Right:**

(1) ICat (UH),

(2) ICat (H),

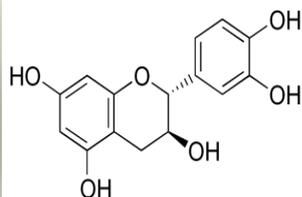
(3) ICat:ODB-2 (UH),

(4) ICat:ODB-2 (H),

(5). BPA:ODB-2 (H).

The sparingly soluble catechin is beige, powdery substance whose melting point was observed at 142 °C. During heating, the catechin turns dark brown. The mixture of catechin and colourant is also light beige. It turns brownish at 130 °C and at 137 °C it changes from dark brown to black. Catechin seems to work as a developer.

### d-Catechin (dCat)



**Left to Right:**

(1) dCat (UH),

(2) dCat (H),

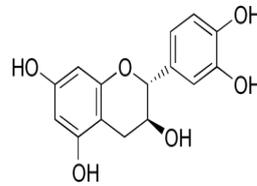
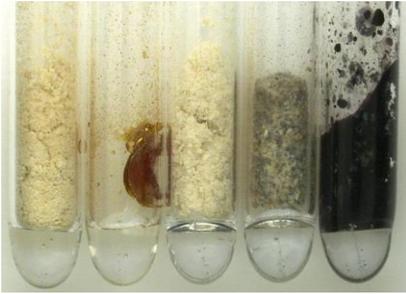
(3) dCat:ODB-2 (UH),

(4) dCat:ODB-2 (H),

(5) BPA:ODB-2 (H).

Similarly, d-catechin is a beige powder that melts at 165 °C and turns orange-red. The near-white mixture of d-catechin and colourant turns black at 134 °C.

### GuaranaCatechin (GCat)



**Left to Right:**

(1) **GCat (UH)**,

(2) **GCat (H)**,

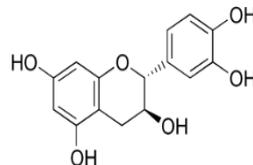
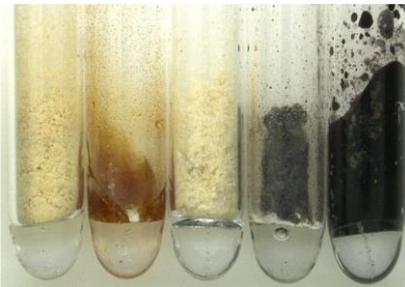
(3) **GCat:ODB-2 (UH)**,

(4) **GCat:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

The results of the rapid test of guarana catechin are almost identical to results obtained from dCat and ICat. However, the melting point determined was 200 °C. During heating, the catechin turned orange-red. The colour of the mixture changed from beige to grey/black at a temperature of 138 °C. The observed dots may be due to the incomplete reaction of Guarana catechin and the colourant. In general the result suggests that Guarana Catechin may function as a developer.

### Acacia Catechin (ACat)



**Left to Right:**

(1) **ACat (UH)**, (2). **ACat (H)**,

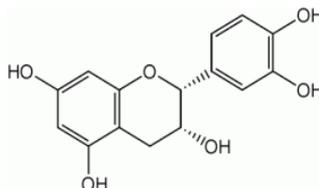
(3) **ACat:ODB-2 (UH)**,

(4) **ACat:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

Acacia catechin gives identical results to the catechin described above. It melts at 198 °C and turns orange-red. The colouring of the mixture occurs at 140 °C. According to this, Acacia-catechin is also potentially usable as a developer.

### l-Epicatechin (ICat)



**Left to Right:**

(1) **ICat (UH)**, (2) **ICat (H)**,

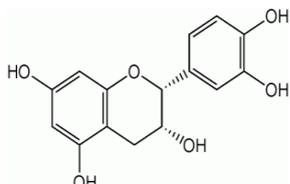
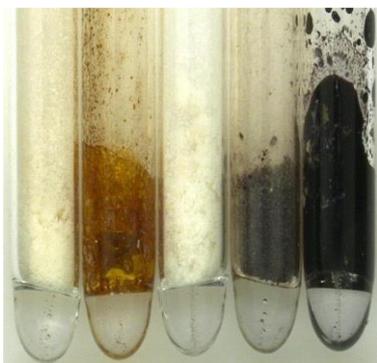
(3) **ICat:ODB-2 (UH)**,

(4). **ICat:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

The light beige, powdery catechin melts at 237 °C and in the process develops an orange-red colour. The mixture of l-epicatechin and colourant is also light coloured. When heated, the mixture slowly turns grey at 170 °C and black at 210-217 °C. In comparison with the reference it is obvious that l-Epicatechin works as a developer.

### (-)-Epicatechin (-ECat)

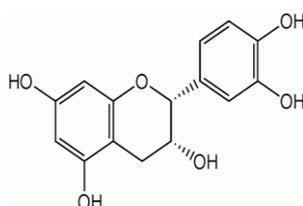
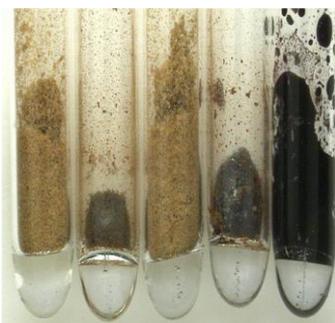


**Left to Right:**

- (1) **ECat (UH)**, (2) **ECat (H)**,
- (3) **ECat:ODB-2 (UH)**,
- (4). **ECat:ODB-2 (H)**,
- (5) **BPA:ODB-2 (H)**.

(-)-Epicatechin is a similar compound to l-Epicatechin. It melts at 230 °C with an orange-red colour change. Colouring occurs at 170 °C and turns black at 210 °C. (-)-Epicatechin works in principle as a developer.

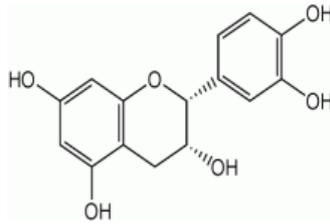
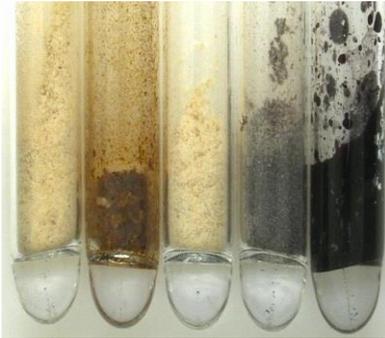
### d-Epicatechin (dECat)



**Left to Right:**

- (1) **dECat (UH)**, (2) **dECat (H)**,
- (3) **dECat:ODB-2 (UH)**,
- (4). **dECat:ODB-2 (H)**, (5) **BPA:ODB-2 (H)**.

Though an Isomer of Epicatechin, d-epicatechin is darker in colour and melts at a significantly lower temperature. In addition, the molten d-epicatechin is also dark in colour. The light brown mixture of d-epicatechin and colourant turns black at 65 °C. Thus, d-Epicatechin also functions in principle as a developer. Since the melting point of d-epicatechin was in a low temperature range, its use as a developer in thermal printers is questionable. In summer, thermal printers often heat up to high temperatures. In this way, the developer might melt through solar radiation alone and initiate the colour reaction. Modification of its physicochemical properties is however, not out of question.

**d-Epicatechin from Gambir (dECatG)**

***Left to Right:***

**(1) dECatG (UH),**

**(2) dECatG (H),**

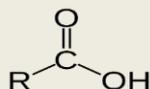
**(3) dECatG:ODB-2 (UH),**

**(4) dECatG:ODB-2 (H),**

**(5) BPA:ODB-2 (H).**

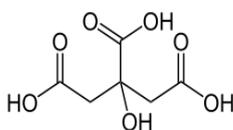
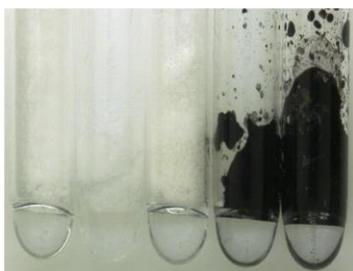
d-Epicatechin extracted from Gambir is a light beige powder. The determined melting point is 228 °C. The mixture of d-epicatechin and colourant gradually turns grey at 165 °C and black at 180-185 °C. As developer d-Epicatechin from Gambir seems to work.

## CARBOXYLIC ACIDS



Carboxylic acids are organic acids with one or more carboxylic groups (-CO<sub>2</sub>H or -COOH) (IUPAC, 1997). Their properties vary significantly with their carbon-chain length. The COOH group is one of the most widely occurring functional groups in chemistry. Carboxylic acids are pervasive in nature.

### Citric Acid (CA)



**Left to Right:**

(1) CA (UH), (2) CA (H),

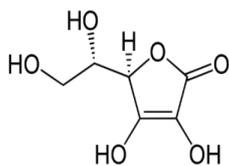
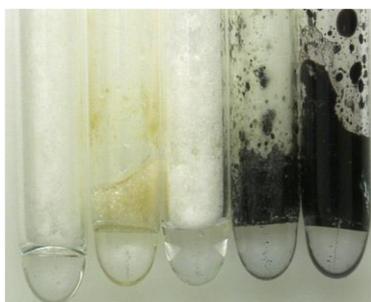
(3) CA : ODB-2 (UH),

(4) CA:ODB-2 (H),

(5). BPA:ODB-2 (H).

Citric acid is a white, powdery substance with a melting point of 150 °C. The mixture of citric acid and colourant turns black when heated at a temperature of 142 °C. In comparison with the reference it should be noted that citric acid leads to the characteristic black colouring. The advantage of this compound is that it has no inherent colour and it is non-carcinogenic. Apart from its solubility in water, nothing stands in the way of using citric acid as a potential developer.

### L-(+)-Ascorbic acid (Asc)



**Left to Right:**

(1) Asc (UH),

(2) Asc (H),

(3) Asc : ODB-2 (UH),

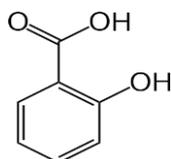
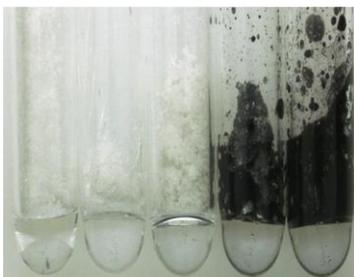
(4) Asc:ODB-2 (H),

(5). BPA:ODB-2 (H).

L-(+)-ascorbic acid is a white, powdery substance. It melts at 189 °C. In the mixture of L-(+)-ascorbic acid and colourant, the colour changes due to the effect of heat at a temperature of 175 °C. This results in the characteristic black colouring. Thus, it seems that L-(+)-ascorbic acid functions as a developer. The colour result and the absence of

inherent colour enhance L-(+)-ascorbic acid's position as a potential developer. L-(+)-ascorbic acid has no known toxicity to man and aquatic organisms (U.S. National Library of Medicine 2015). It is also not carcinogenic. Accordingly, L-(+)-ascorbic acid is suitable as a developer.

### Salicylic acid (SA)



**Left to Right:**

(1) SA (UH), (2). SA (H),

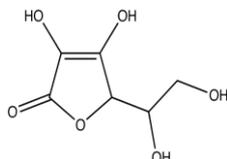
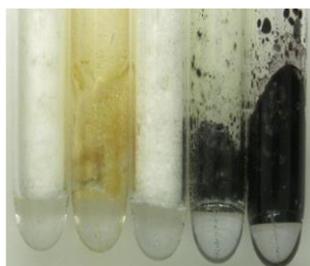
(3) SA:ODB-2 (UH),

(4) SA:ODB-2 (H),

(5) BPA:ODB-2 (H)

The white powdery substance salicylic acid melts at 158 °C. The mixture of salicylic acid and colourant is also white and turns black when heated. The colouring occurs at a temperature of 115 °C. Salicylic acid seems to work as a developer compared to the reference. Salicylic acid is poorly soluble in cold water (20 °C) and more easily soluble in warm water (80 °C). It is non-carcinogenic. The non-toxic nature of salicylic acid makes its use as a developer quite conceivable.

### Ascorbic Acid (AsA)



**Left to Right:**

(1) AsA (UH), (2). AsA (H),

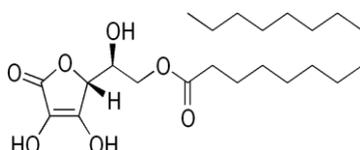
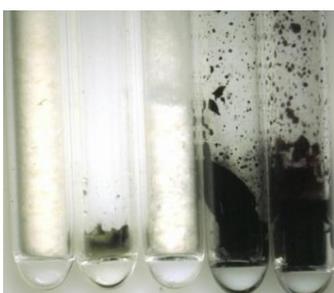
(3). AsA:ODB-2 (UH),

(4). AsA:ODB-2 (H),

(5). BPA:ODB-2 (H).

Ascorbic acid has no inherent colour. It melts at 189 °C. In combination with the colourant, the colour white changes to black at a temperature of 178 °C under the influence of heat. The result is also similar to that observed with L-(+)-ascorbic acid.

### 6-O-Palmitoyl L-ascorbic acid (Ascorbyl Palmitate) (6-OPAs)



**Left to Right:**

(1) 6-OPAs (UH),

(2) 6-OPAs (H),

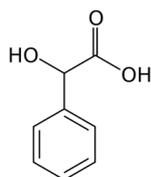
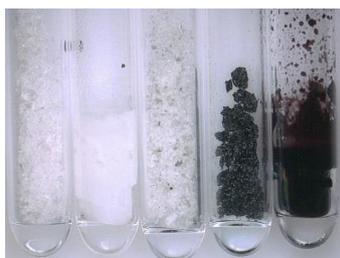
(3) 6-OPAs:ODB-2 (UH),

(4) 6-OPAs:ODB-2 (H),

(5) BPA:ODB-2 (H).

Ascorbyl Palmitate, an ester formed from ascorbic acid and palmitic acid, is a fat soluble white substance which melts between 115°C and 120°C and turns slightly dark in the process. The mixture of Ascorbyl Palmitate and colourant is white and produces an intense black colour on heating to about 100°C. Based on this observation, Ascorbyl Palmitate seems to work as a developer.

### Mandelic Acid (MA)



**Left to Right:**

(1) MA (UH), (2) MA (H),

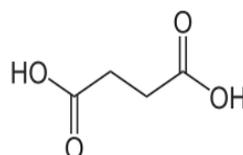
(3) MA:ODB-2 (UH),

(4) MA:ODB-2 (H),

(5) MA:ODB-2 (H).

Mandelic acid is a white crystalline solid. It melts at about 120°C. The simple mixture of mandelic acid and colourant gave a clearly unmixed white product with apparent black dots. On heating, the mixture turned dark. It doesn't seem that the mixture melts but the black colour formation suggests a reaction occur, making mandelic acid a potential developer.

### Succinic Acid (SA)



**Left to Right:**

(1) SA (UH), (2) SA (H),

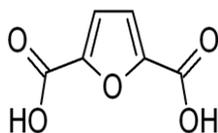
(3) SA:ODB-2 (UH),

(4) SA:ODB-2 (H), (5) BPA:ODB-2 (H).

Succinic acid, a white solid melted at 180-185°C. On cooling, the molten sample turns cloudy. The whitish appearance remains unchanged when mixed with the colourant. On heating at about 125°C, the mixture turned black with a glassy appearance. Succinic acid is a dibasic, which can undergo deprotonation. This deprotonation may account for the black colour formation and thus making succinic acid a potential developer. Succinic acid is classified as one of the top 12 biomolecules (DOE) by the US Department of Energy Efficiency and Renewable Energy (NREL 2004).

## 2,5-FURAN DICARBOXYLIC ACID (2,5-FDCA)

2,5-Furandicarboxylic acid is an organic compound with two carboxylic groups attached to a central furan ring. It can be produced from certain carbohydrates and as such is a renewable resource.



### *Left to Right:*

(1) 2,5-FDCA (UH),

(2) 2,5-FDCA (H),

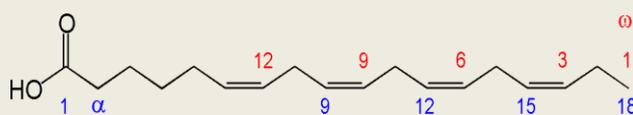
(3) 2,5-FDCA:ODB-2 (UH),

(4) 2,5-FDCA:ODB-2 (H),

(5) BPA:ODB-2 (H).

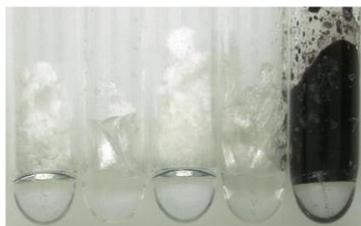
2,5-FDCA is off white in appearance. Though it shows a little darkening when heated to a high temperature, its melting point (342°C) couldn't be ascertained with the rapid screening method. The mixture of 2,5-FDCA and the colouring agent also takes the colour of the pure sample. On heating, a black colour develops at about 150°C. Surprisingly, the 2,5-FDCA did not melt at 150°C but produces a colour with the colouring agent. It is understood that the carboxylic groups may be readily available for reaction but this observation is quite curious and would require a further investigation. The fact that 2,5-FDCA is a renewable material makes it a promising candidate as a developer either as a pure sample or in modified form.

## FATTY ACID

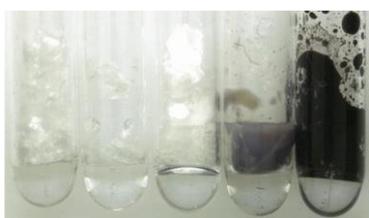


Fatty acids are carboxylic acids with long aliphatic chains. Fatty acids occur naturally in plants and animals and can also be synthesised.

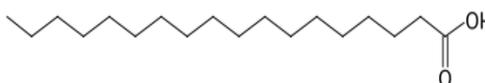
### Stearic acid (StA)



(a)



(b)



**Left to Right:**

(1) StA (UH),

(2) StA (H),

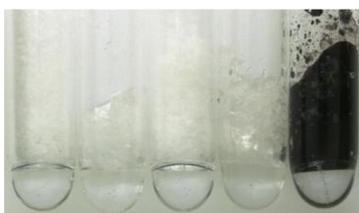
(3) StA:ODB-2 (UH),

(4) StA:ODB-2 (H),

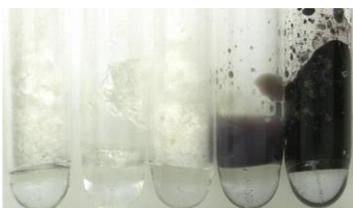
(5) BPA:ODB-2 (H).

Stearic acid is a powdery white substance with a melting point of 70°C. The mixture of stearic acid and colourant remains white. No colour change takes place during mixing in the rapid test. The mixture melted at a temperature of 70 °C and up to 85 °C without any change in colouration (a). Because no colour change was observed in the rapid test, the mixture was heated to higher temperatures. Apparently a higher temperature of about 190°C was necessary to develop the purple colour (b). According to Orihara *et al* (2012) stearic acid can be used as a colour developer simply because of its function as a proton donor.

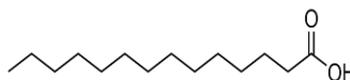
### Myristic Acid (MyA)



(a)



(b)



**Left to Right:**

(1) MyA (UH),

(2). MyA (H),

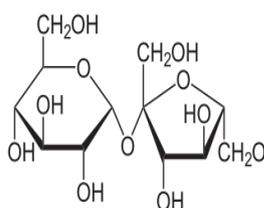
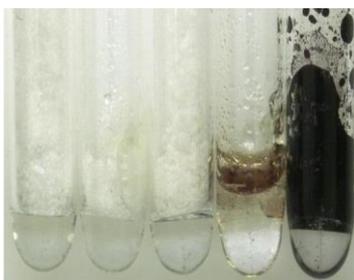
(3). MyA:ODB-2 (UH),

(4). MyA:ODB-2 (H),

(5) BPA:ODB-2 (H).



## Sucrose



**Left to Right:**

(1) **Sucrose (UH)**, (2) **Sucrose (H)**,

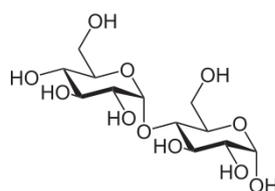
(3) **Sucrose:ODB-2 (UH)**,

(4) **Sucrose:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

Similarly to Glucose, Sucrose shows no colour reaction with the colouring agent.

## Maltose



**Left to Right:**

(1) **Maltose (UH)**, (2) **Maltose (H)**,

(3) **Maltose:ODB-2 (UH)**,

(4) **Maltose:ODB-2 (H)**,

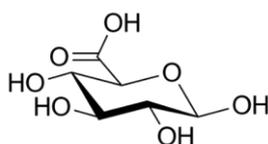
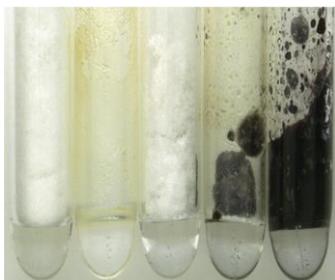
(5) **Maltose:ODB-2 (H)**.

Maltose monohydrate, a white powdery disaccharide melted at 165°C. Mixture of maltose and colourant remains white but changes to a burnt black colour when heated to 150°C. This burnt black colouration suggests a degradation of Maltose rather than a colour reaction. Maltose is a reducing sugar and may work as a developer but further modification may be necessary to adjust its chemical properties.

## SUGAR ACID

Sugar acids are monosaccharides with a carboxyl group.

### Glucuronic acid (GU)



**Left to Right:**

(1) **GU (UH)**, (2) **GU (H)**,

(3) **GU:ODB-2 (UH)**,

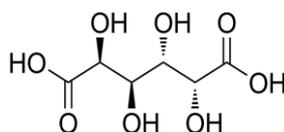
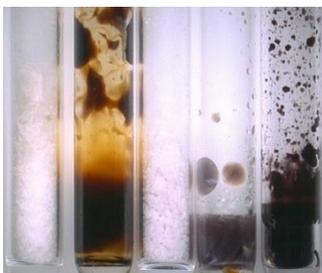
(4) **GU:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

D-glucuronic acid is a white, powdery substance that melted in a rapid test at a temperature of 165 °C. The colour change of the mixture begins in the quick test at a

temperature of 160 °C to change from white to gray. The black colour of the mixture appears at a temperature of 172 °C. In comparison with the reference D-glucuronic acid functions as a developer. Though, it is a water-soluble compound, D-glucuronic acid has no carcinogenic effect on humans.

### Mucic Acid (MuA)



*Left to Right:*

(1) **MuA (UH)**, (2) **MuA (H)**,

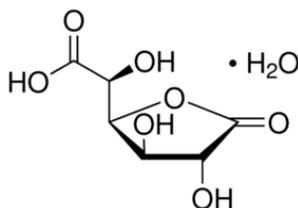
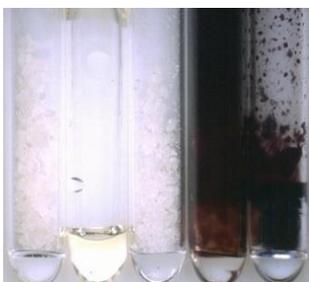
(3) **MuA:ODB-2 (UH)**,

(4) **MuA:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

Mucic acid is a white powdery sugar compound. At temperature beyond 220°C the acid substance begins to melt producing a burnt black colouration. Below 200°C no physical change is observed. Mixture of mucic acid and colourant is off white and turns fade black on heating to about 200°C. Mucic acid seems to work as a developer.

### D-Saccharic acid 1,4-lactone monohydrate (DSL)



*Left to Right:*

(1) **DSL (UH)**, (2) **DSL (H)**,

(3) **DSL:ODB-2 (UH)**,

(4) **DSL:ODB-2 (H)**,

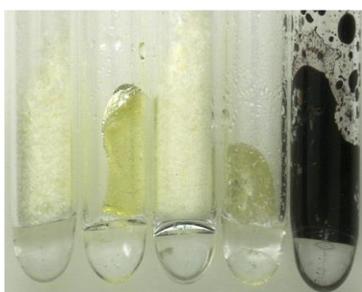
(5) **BPA:ODB-2 (H)**.

Saccharic acid lactone is a white solid crystal. The crystal melts at about 85°C to produce a white transparent liquid. Mixture of the solid sample and colourant remains white. On heating, the mixture turns black at about 90°C. In comparison to the reference, saccharic acid lactone looks promising as a developer.

## ROSIN

Rosin also known as colophony is a solid form of resin obtained from pines and some other plants. Rosin is an ingredient in printing inks, photocopying and laser printing paper, adhesives, paper sizing and sealing wax.

### Colophony



#### *Left to Right:*

(1) Rosin (UH), (2) Rosin (H),

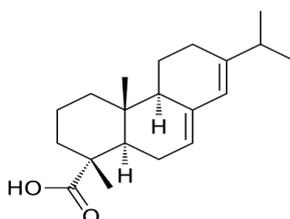
(3) Rosin:ODB-2 (UH),

(4) Rosin:ODB-2 (H),

(5) BPA:ODB-2 (H).

Colophony is a white-yellowish mixture of substances whose melting point was achieved at about 84°C. The mixture of rosin and colourant melts at about 80 °C without any colour change. Colophony does not work as a developer compared to the reference. The reason for this may be that rosin was not in the acid form. Proton release is not possible in the esterified form.

### Abietic Acid (AA)



#### *Left to Right:*

(1) AA (UH), (2) AA (H),

(3) AA:ODB-2 (UH),

(4) AA:ODB-2 (H),

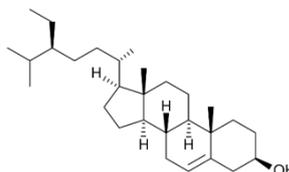
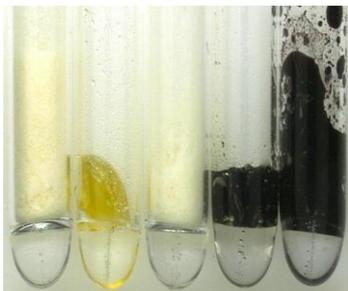
(5) BPA:ODB-2 (H).

Abietic acid is a crystalline yellow solid. Its melting was observed when heated above 150°C. The yellow colour remains unchanged when mixed with the colourant. Under heat, the mixture turns deep black suggesting a reaction between abietic acid and the colourant. This colour formation is similar to the reference. In principle, abietic acid could function as a developer. Moreover, it is considered a 'nonhazardous natural substances' in tall oil (Norlin 2002).

## PHYTOSTEROLS

Phytosterols belong to the class of sterols commonly found in plants.

### $\beta$ -sitosterol ( $\beta$ st)



*Left to Right:*

(1)  $\beta$ st (UH), (2)  $\beta$ st (H),

(3)  $\beta$ st:ODB-2 (UH),

(4)  $\beta$ st:ODB-2 (H),

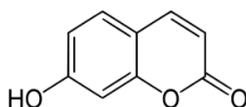
(5) BPA:ODB-2 (H).

The  $\beta$  sitosterol is light beige to white solid in appearance. It melts at 140 °C. The mixture of  $\beta$ -sitosterol and colourant remains beige unheated but turns black at a temperature of 150°C.  $\beta$ -Sitosterin seems to work as a developer.  $\beta$ -Sitosterol is not carcinogenic for humans. Its full toxicity potential is unclear (Sigma-Aldrich 2015f). This suggests that  $\beta$ -sitosterol could be used as a developer.

## COUMARINS

Coumarins are organic compounds which belongs to the Coumarin family found natural in many plants

### Umbelliferone



*Left to Right:*

(1) Umb (UH), (2) Umb (H),

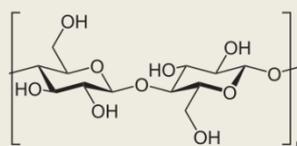
(3) Umb:ODB-2 (UH),

(4) Umb:ODB-2 (H),

(5) BPA:ODB-2 (H)

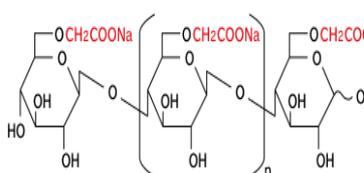
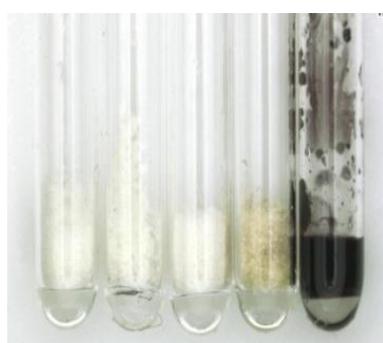
Umbelliferone is a light beige powder. When heated, it melted at a temperature of 230°C. The mixture of the two components colourant and potential developer gradually turns grey and finally black when heated. Discolouration begins at 155°C and continues at 180°C. Umbelliferone therefore acts as a colour developer. Umbelliferone is not carcinogenic for humans and hardly soluble in water.

## CELLULOSE ETHER



Cellulose ethers are polymers produced by the chemical modification of cellulose. Cellulose and its derivatives are environmentally friendly, as they are degradable by several bacteria and fungi present in air, water and soil. They are polysaccharides of high molecular weight which does not possess skin absorption problem associated with BPA.

### Sodium Carboxymethylcellulose (Na-CMC)



**Left to Right:**

(1) NaCMC (UH),

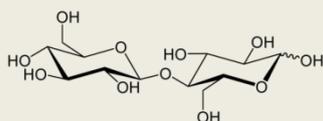
(2) NaCMC (H),

(3) NaCMC:ODB-2 (UH),

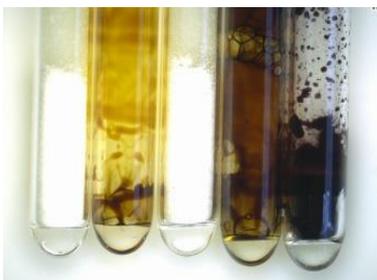
(4) NaCMC:ODB-2 (H),

(5) NaCMC:ODB-2 (H).

The colourant produces a white mixture with the colourless, solid substance Na-CMC. When heated, only the colourant melted at a temperature of 179 °C, at higher temperatures (up to 230 °C) nothing more happens. Na-CMC does not seem to work as a potential developer. Apparently the hydroxy groups of cellulose are completely substituted with sodium-carboxymethyl groups, so that there were no more groups with acid function. No proton could be released and the colourant could not change from the colourless to the coloured state. It is therefore not surprising that the sodium salt of CMC does not function as a developer. Thus, the rapid test with the acid form of CMC would probably have made more sense. For this reason, Na-CMC was hydrolyzed in the course of the work in an acidic medium and tested for its potential efficacy in a rapid test. The result is reported under AP3.

**CELLOBIOSE**

Cellobiose is a disaccharide and reducing sugar consisting of two  $\beta$ -glucose molecules linked by a  $\beta(1-4)$  bond. Cellobiose has eight free alcohol (OH) groups, once acetal linked and one hemiacetal linkage which give rise to strong inter-and intramolecular hydrogen bonds.

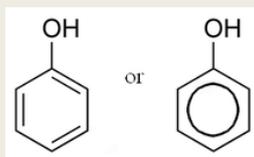
**Cellobiose**

***Left to Right:***

- (1) Cellobiose (UH),**
- (2) Cellobiose (H), (3) Cellobiose:ODB-2 (UH),**
- (4) Cellobiose:ODB-2 (H),**
- (5) Cellobiose:ODB-2 (H).**

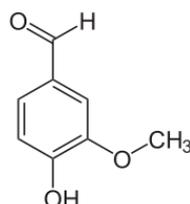
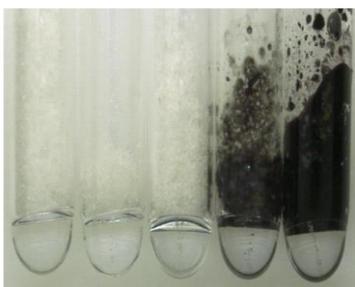
Cellobiose is crystal whitish in appearance. It melted at a temperature about 200°C. The brownish colour produced suggests decomposition typical of cellulosic compounds. The mixture of cellobiose and the colouring agent remains colourless until heated to about 180°C. A brownish-black colour (similar to burnt appearance) is produced. The colour formed remains unchanged at about 230°C. Cellobiose is a natural compound but the above result does not suggest a colour reaction with the colouring agent and thus may not function as a developer. Modification of cellobiose may give rise to product of better functionality.

## MONOMERIC PHENOLIC COMPOUNDS



Monomeric phenolic compounds are naturally occurring phenolic compounds which are commonly found in plants and forms part of the lignin degradation products.

### Vanillin



**Left to Right:**

(1) **Vanillin (UH)**, (2) **Vanillin (H)**,

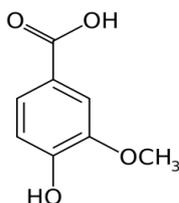
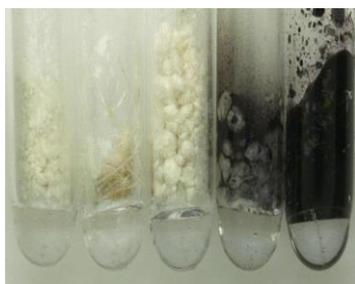
(3) **Vanillin:ODB-2 (UH)**,

(4) **Vanillin:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

Vanillin is colourless and melted in the rapid test at a temperature of 82°C. When heated, the mixture of vanillin and colourant turns black at a temperature of 81-82°C. The developed black colour has a purple hue. Vanillin, in principle, seems to work as a developer. This makes Vanillin a suitable candidate as a developer in thermal paper. The LD50 value, determined by oral administration to rats, is 3,300 mg/kg. Vanillin is not carcinogenic in humans and only slightly soluble in water (GESTIS substance database).

### Vanillic Acid (VA)



**Left to Right:**

(1) **VA (UH)**, (2) **VA (H)**,

(3) **VA:ODB-2 (UH)**,

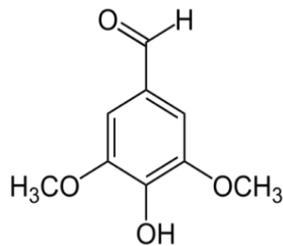
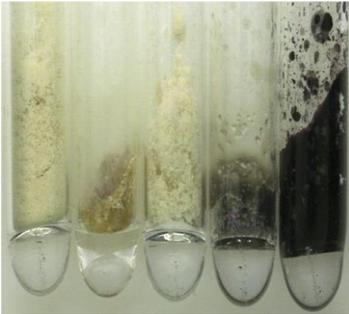
(4) **VA:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

The light beige powder vanillic acid melted at a temperature of 212°C. The mixture of colourant and vanillic acid gradually discoloured at a temperature of 168°C. Heating of the mixture was stopped at 195°C. In comparison with the reference it becomes clear that vanillic acid basically functions as a developer. After taking all other important properties into account, including solubility in water and toxicity, vanillic acid fulfils all

criteria of a potential developer.

### Syringaldehyde (Sy)



**Left to Right:**

(1) Sy (UH), (2) Sy (H),

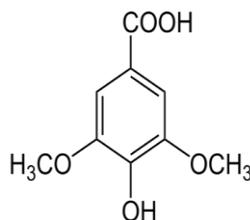
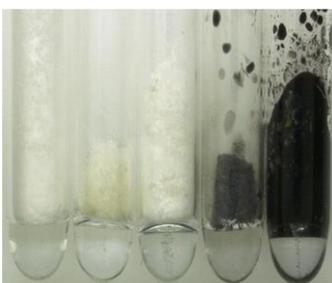
(3) Sy:ODB-2 (UH),

(4) Sy:ODB-2 (H),

(5) BPA:ODB-2 (H).

Syringaldehyde is a beige-white powder in appearance and melted at a temperature of 113°C. When heated, the light mixture of syringaldehyde and colourant turns dark green. The colour change takes place in a temperature range of 113°C to 118°C. Syringaldehyde basically functions as a colour developer. According to the PBT profiler classification, syringaldehyde is an environmentally friendly compound (PBT). At 9.5 mg/l water, syringaldehyde is just below the level in which no negative effects have been identified for fish. An LD50 value of 1,000 mg/kg was found. This value was determined by intraperitoneal administration in mice. Since intraperitoneal administration was not classified by the EPA and no other LD50 value was found, it cannot be clearly determined whether syringaldehyde is harmless in this respect. Syringaldehyde is also insoluble in water.

### Syringic Acid



**Left to Right:**

(1) SyA (UH), (2) SyA (H),

(3) SyA:ODB-2 (UH),

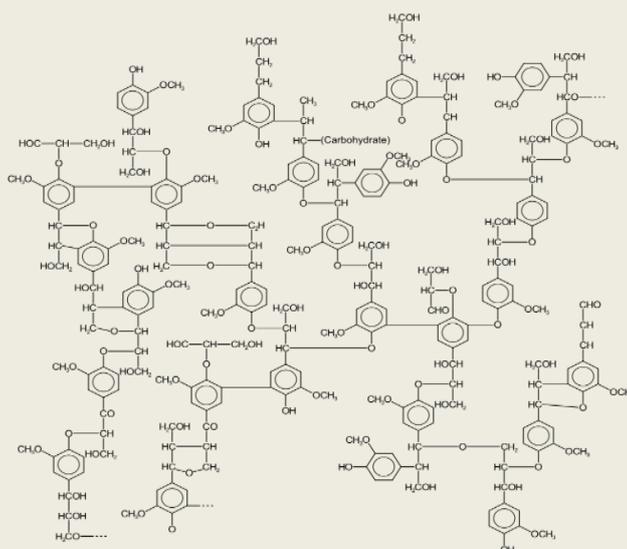
(4) SyA:ODB-2 (H),

(5) BPA:ODB-2 (H).

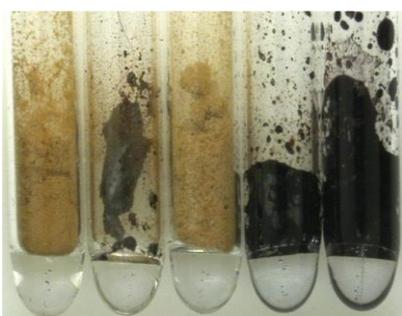
The beige powder of syringic acid has a determined melting point of 207 °C. The mixture of syringic acid and colourant turns black during heating. The black has a purple stitch. The staining occurs at a temperature of 179°C and was completed at 205°C. The PBT profile of syringic acid is PBT, which makes syringic acid conceivable as a developer according to PBT criteria. Only 100 mg/l water is toxic for fish. Syringic acid is not carcinogenic to humans.

## LIGNIN

Lignin is a class of complex organic polymers that form structural materials in the support tissue of vascular plants (Martone, 2009). Lignins are crosslinked phenolic polymers, which are major component of wood and bark. In recent times, isolation and purification of lignin from wood processing by-product – black liquor – has increased. This natural raw material is seen as a source of various monomeric and macromolecular materials both synthetic and natural.



### Pyrolysis lignin from beech (PylB)



**Left to Right:**

**(1) PylB (UH),**

**(2) PylB (H),**

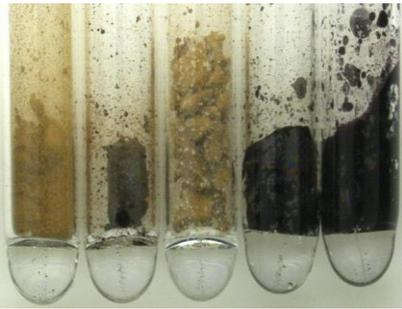
**(3) PylB:ODB-2 (UH),**

**(4) PylB:ODB-2 (H),**

**(5) BPA:ODB-2 (H).**

The beech pyrolysed lignin has a medium brown colour and a powdery consistency. When heated, it turns darker at a temperature of about 130 °C. The pyrolysis lignin was heated to 230 °C. The mixture of pyrolysis lignin (beech) and colourant also turns black when heated. The colour change from light brown to black begins at a temperature of 135 °C and persists at 170 °C. The beech pyrolyse lignin seems to work as a developer. There was even a black colouration without addition of the colourant. The phenolic compounds in the lignin structure may be responsible for the colouration.

### Pyrolysis lignin from spruce/fir (PylS)



**Left to Right:**

(1) PylS (UH),

(2) PylS (H),

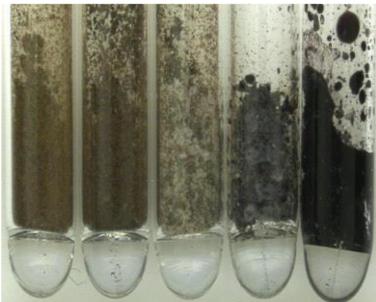
(3) PylS:ODB-2 (UH),

(4) PylS:ODB-2 (H),

(5) BPA:ODB-2 (H).

The spruce/fir pyrolysis lignin has a slightly darker brown tone compared to beech. The colouring of the spruce pyrolysis lignin also starts at a temperature of about 130°C during heating. At 230°C the heating of the pyrolysis lignin was stopped. The black colouration of the mixture takes place at a temperature range of 130-150°C. The spruce pyrolysis lignin also seems to work in comparison with the reference. And even with this pyrolysis lignin, the addition of the colourant was not necessary to produce a black colour.

### HTC Straw lignin



**Left to Right:**

(1) HTC (UH), (2) HTC (H),

(3) HTC:ODB-2 (UH),

(4) HTC:ODB-2 (H),

(5) BPA:ODB-2 (H).

The HTC straw lignin is heated up to a temperature of 180°C using the rapid test method. The brown colour becomes slightly darker. The mixture of HTC straw lignin with the colourant turns black at 183 °C. In comparison with the reference, HTC straw lignin also seems to function as a potential developer.

### Organosolv Lignin (OrgL)



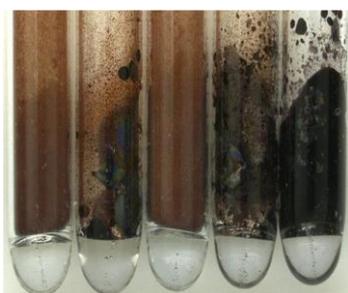
**Left to Right:**

(1) OrgL (UH), (2) OrgL (H),

(3) OrgL:ODB-2 (UH), (4) OrgL:ODB-2 (H), (5) BPA:ODB-2 (H).

The medium-brown high-molecular organosolv lignin precipitated from organosolv liquor (**AP2**) becomes darker when heated at temperatures of 150°C and above. The colour shown above was obtained at 175°C. The powdered mixture of organosolv lignin and colourant also turns darker at a temperature of 150°C and above. At 179°C the colourant melts and the mixture turns completely black. The organosolv lignin seems to contain components that can mimic the function of a developer because it also turns black when heated without the addition of the colourant. According to Puls (2009), technical lignins differ in the number of their phenolic hydroxy groups. Organosolv lignins have many phenolic hydroxy groups compared to lignosulfonates and sodalignins, which increases the ability to react as a potential developer.

### Beech sulfate lignin (BSL)



**Left to Right:**

(1) **BSL (UH)**,

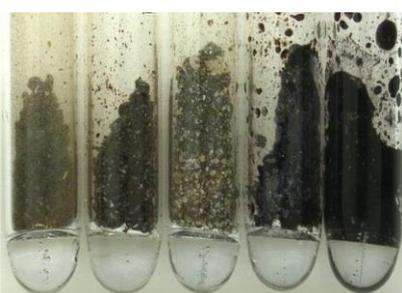
(2) **BSL (H)**,

(3) **BSL:ODB-2 (UH)**,

(4) **BSL:ODB-2 (H)**,

The beech sulphate lignin was precipitated from beech sulphate liquor (**AP2**). The high-molecular weight lignin from beech sulphate liquor is dark brown powder in appearance and becomes darker when heated within a temperature range of 150-162°C. The mixture of beech sulfate lignin and colourant turns black when heated to 140-173°C. The beech sulfate lignin thus functions as a developer and also causes a black colour change without the addition of colourants. According to Dimmel and Gellerstedt (2010), sulfate lignins have additional phenolic hydroxy groups due to the cleavage of the  $\beta$ -O-4 bonds during the digestion process. This property increases the effect of sulphate lignins as potential developers.

### Pine sulphate lignin (PSL)



**Left to Right:**

(1) **PSL (UH)**, (2) **PSL (H)**,

(3) **PSL:ODB-2 (UH)**, (4) **PSL:ODB-2 (H)**,

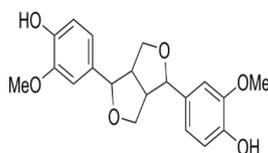
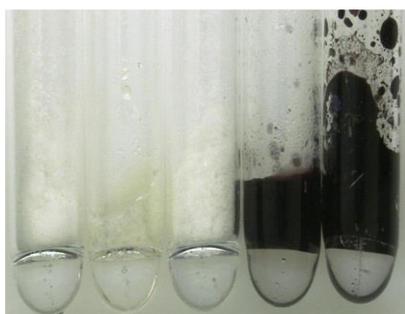
(5) **BPA:ODB-2 (H)**.

Pine sulfate lignin is the high-molecular lignin from pine sulfate liquor (**AP2**). The dark brown coloured pine sulfate lignin turns darker at a temperature range of 165-185°C. The mixture of pine sulfate lignin and colourant changed colour from a temperature of 170°C and was coloured completely black at 179°C. The pine sulfate lignin seems to function as a developer. Black colouration was also achieved without the addition of the colourant. According to Fischer and Wienhaus (1982), sulfate lignins from softwood have more phenolic hydroxy and carbonyl groups but less aliphatic hydroxy and methoxy groups than protolignin. These conditions enhance the effect as a colour developer.

## LIGNAN

Lignans are large groups of polyphenols found naturally in plant.

### d-l-Pinoresinol



#### *Left to Right:*

(1) **d-l-P (UH)**,

(2) **d-l-P (H)**,

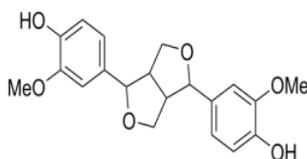
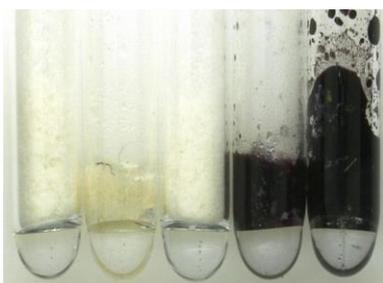
(3) **d-l-P:ODB-2 (UH)**,

(4) **d-l-P:ODB-2 (H)**,

(5) **BPA:ODB-2 (H)**.

d-l-Pinoresinol, an isomer of raw Pinoresinol is a white, powdery substance. The d and l forms of Pinoresinol are present in this sample. d-l-pinoresinol melts at 150 °C. The mixture of d-l-pinoresinol and colourant melts and turns black when heated at a temperature of 143°C. The black colour developed shortly after the heating was stopped. As a developer, d-l-pinoresinol seems to work with it. In addition, the black colour has a purple hue, just as with the reference. d-l-Pinoresinol is slightly water-soluble and is not carcinogenic. Since lignans are phytoestrogens, their use as developers may need further critical evaluation. The estrogenic activity of phytoestrogens can have positive effects, for example with regard to hormone-dependent cancers. However, negative effects of phytoestrogens have also been observed in animal experiments. To what extent the results of these studies can be transferred to humans still remains unclear (Dräger 2015).

## Raw Pinoresinol



***Left to Right:***

**(1) Pinoresinol (UH),**

**(2) Pinoresinol (H),**

**(3) Pinoresinol:ODB-2 (UH),**

**(4) Pinoresinol:ODB-2 (H),**

**(5) BPA:ODB-2 (H).**

The raw Pinoresinol is white-yellowish in appearance and melted at 151 °C. The mixture behaves in the rapid test same way as d-l-pinoresinol. The colour change occurs when the two components melted, but the black colour does not develop until the heating is stopped. The two components melts at a temperature of 135°C. Since the crude pinoresinol is only a less purified form of pinoresinol, the property evaluation d-l-pinoresinol also applies.

## LOW MOLECULAR PHENOLIC COMPOUNDS

These are phenolic compounds left after the isolation of the high molecular weight lignin fraction. More details are provided under AP2.

### Organosolv Extract



***Left to Right:***

**(1) OrgExt (UH), (2) OrgExt (H),**

**(3) OrgExt:ODB-2 (UH),**

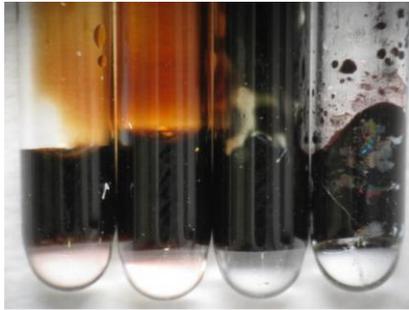
**(4) OrgExt:ODB-2 (H),**

**(5) BPA:ODB-2 (H).**

The organosolv extract appears as an orange-red viscous liquid. Under the influence of heat, it became steadily dark at a temperature of 180°C. The heating takes place up to a temperature of 230°C. The mixture of organosolv extract and colourant turns black at 55 °C. In comparison with the reference, it is noticeable that both the mixture and the extract alone changes colour on heating. The extract therefore contains components that have the developer function. Since the extract also leads to a black colour change into

without adding the colourant, further tests have to be carried out to see to what extent the extract could be fractionated so that it would lose its inherent colour and still contain the components that produce the colour on heating.

### Beech Sulfate Extract (BsExt)



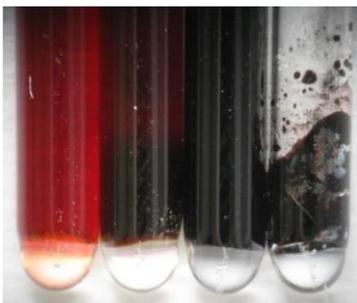
***Left to Right:***

**(1) BsExt (UH), (2) BsExt (H),**

**(3) BsExt:ODB-2 (UH), (4) BsExt:ODB-2 (H) , (5) BPA:ODB-2 (H).**

The untreated beech sulphate extract is already very dark in colour. When heated, the beech sulphate extract turns only slightly darker. The black colour of the mixture of colourant and beech sulfate extract develops by simply mixing the two components. When heated up to 120°C, the colour of the mixture was no longer clearly intensified. Thus, the beech sulfate extract also contains components that have the function of a developer. The fact that the colouring did not require any heat exposure is probably due to the liquid consistency of the extract.

### Pine sulphate extract (PsExt)



***Left to Right:***

**(1) PsExt (UH),**

**(2) PsExt (H),**

**(3) PsExt:ODB-2 (UH),**

**(4) PsExt:ODB-2 (H) ,**

**(5) BPA:ODB-2 (H).**

The pine sulphate extract is reddish in colour and, like the two other extracts, has a viscous consistency. When heated up to a temperature of 230°C, the extract turns black. The mixture of pine sulphate extract and colouring agent also turns black by mixing together just like the beech sulphate extract. The black intensifies when the mixture was heated to a temperature of 100°C. This extract also seems to work as a developer

## AP1.2 Dye-Developer Interaction.

### AP1.2.1. Acetone Test

To supplement the rapid screening method, selected compounds were subjected to acetone test. This test allows for the study of the dye-developer **interaction between ODB-2, and developer** (Rihs and Weis 1991). 0.00532 g, 0.01 mmol ODB-2 was added to 20 ml acetone. Unless otherwise stated, 0.04 mmol of screened substance was added to the mixture and allowed to stand for 5 days. Acetone was removed via rotary evaporation and the solid black crystal was stored in a glass bottle. In the case of Tannin and catechin, 20 mg of the substance was mixed with 10 mg of ODB-2 in acetone. Results of the acetone test (Figure 6) show that all studied compounds produce black colour with the ODB-2. Colourless mixture was earlier obtained but turned black after evaporation of acetone. FTIR of the black crystals was recorded on a Bruker Vector 33 instrument from 3750 to 530  $\text{cm}^{-1}$  with 60 cumulative scans and a resolution of 4  $\text{cm}^{-1}$ .



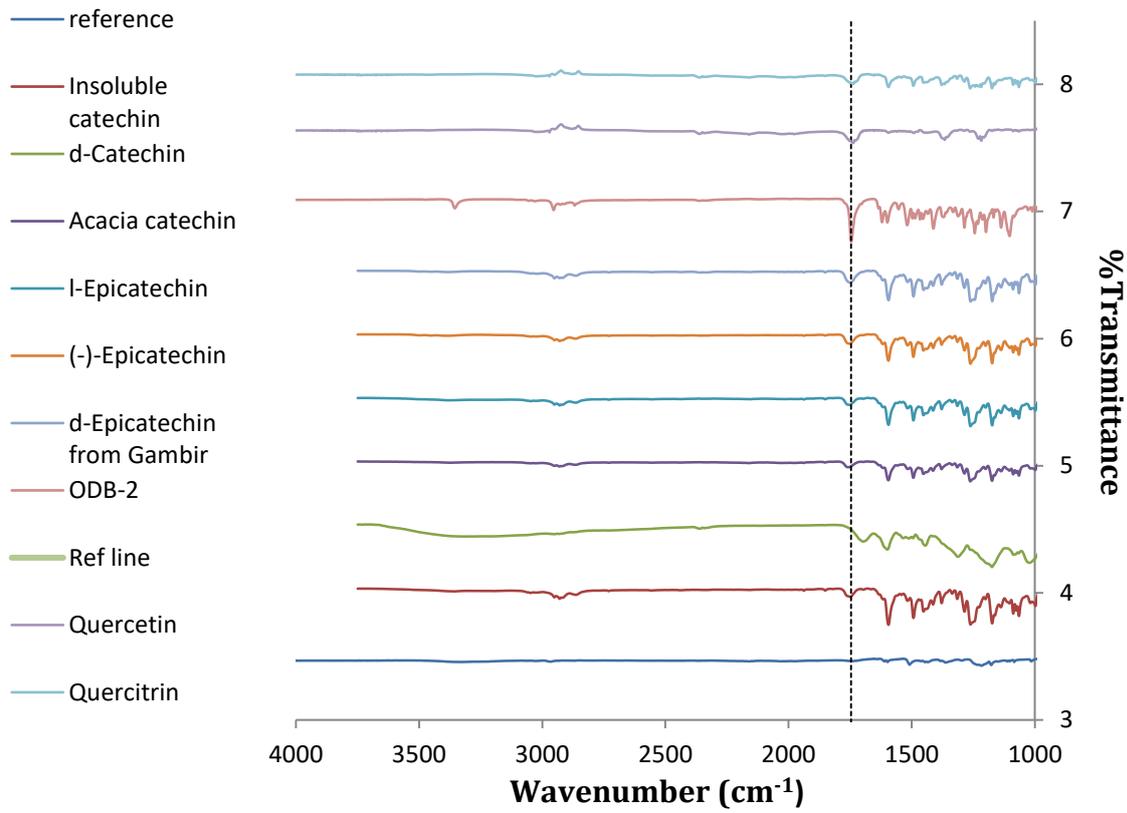
Figure 6. Results of acetone test

**AP1.2.2. Fourier Transform Infra-red Spectroscopy (FTIR)**

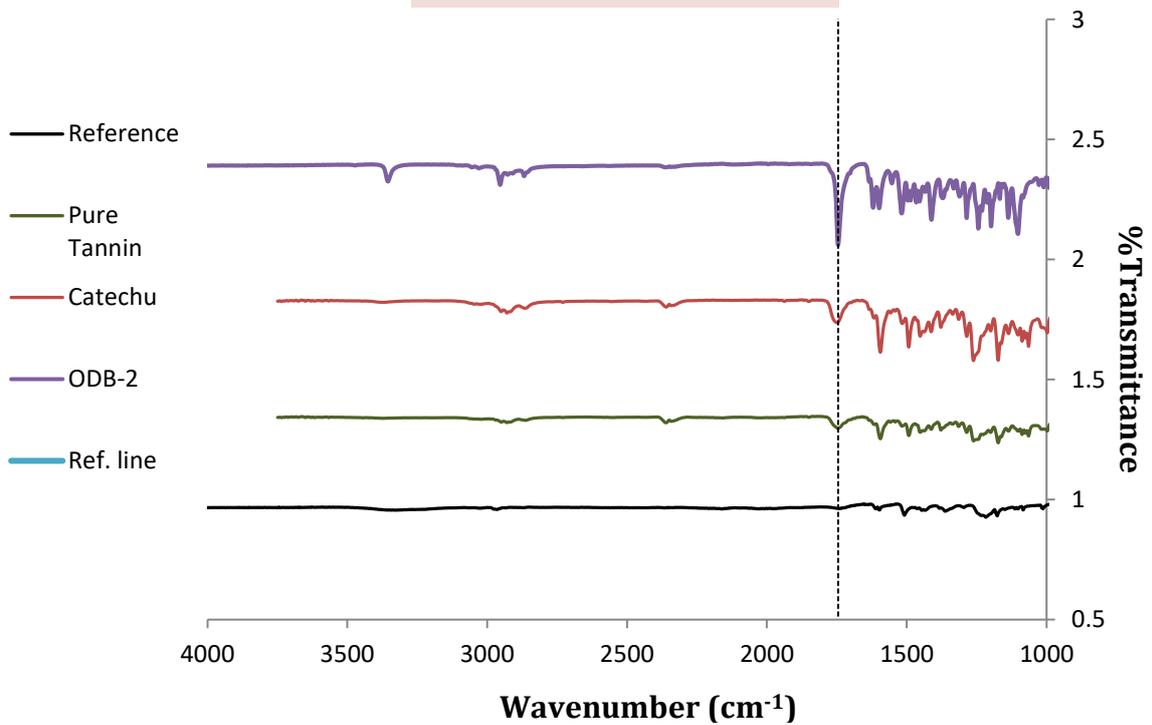
The reaction between the tested samples and the colouring agent, ODB-2 dye was further investigated by FT-IR spectroscopy (Figure 7) using the ATR method.

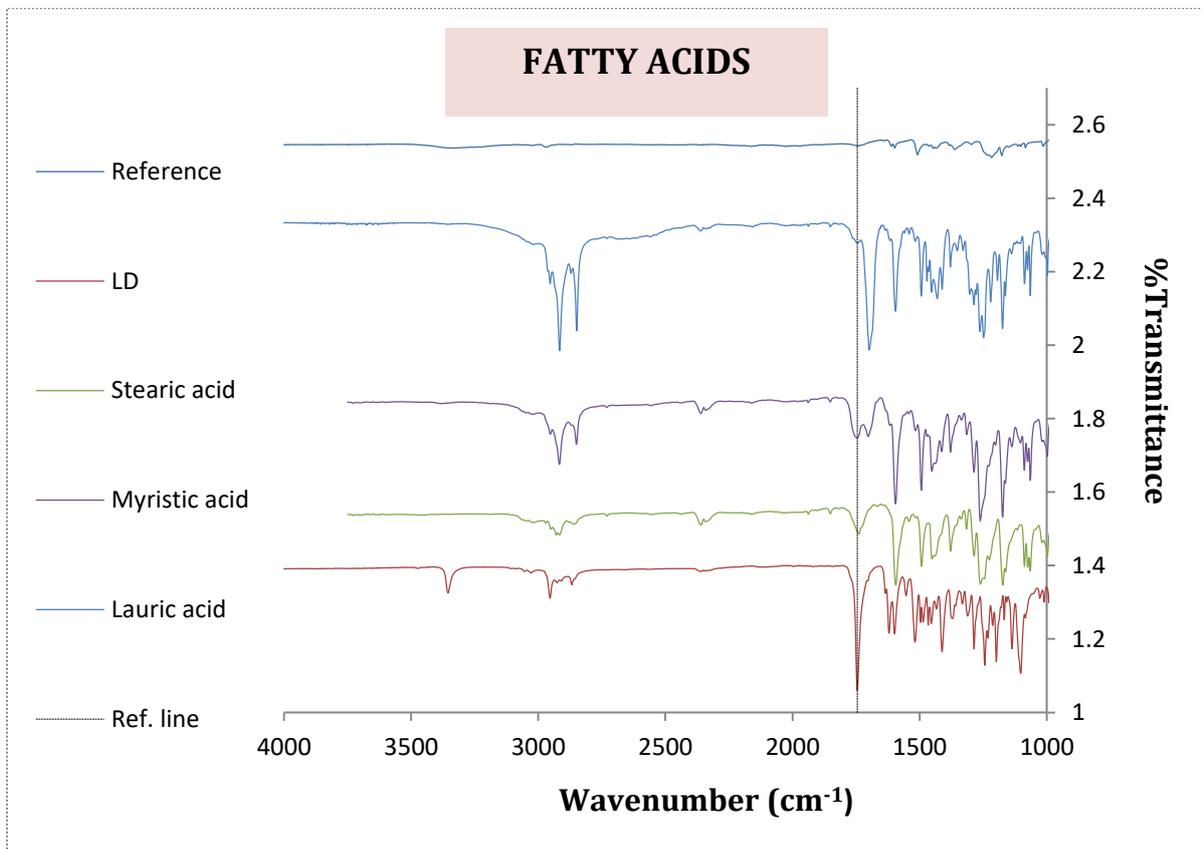
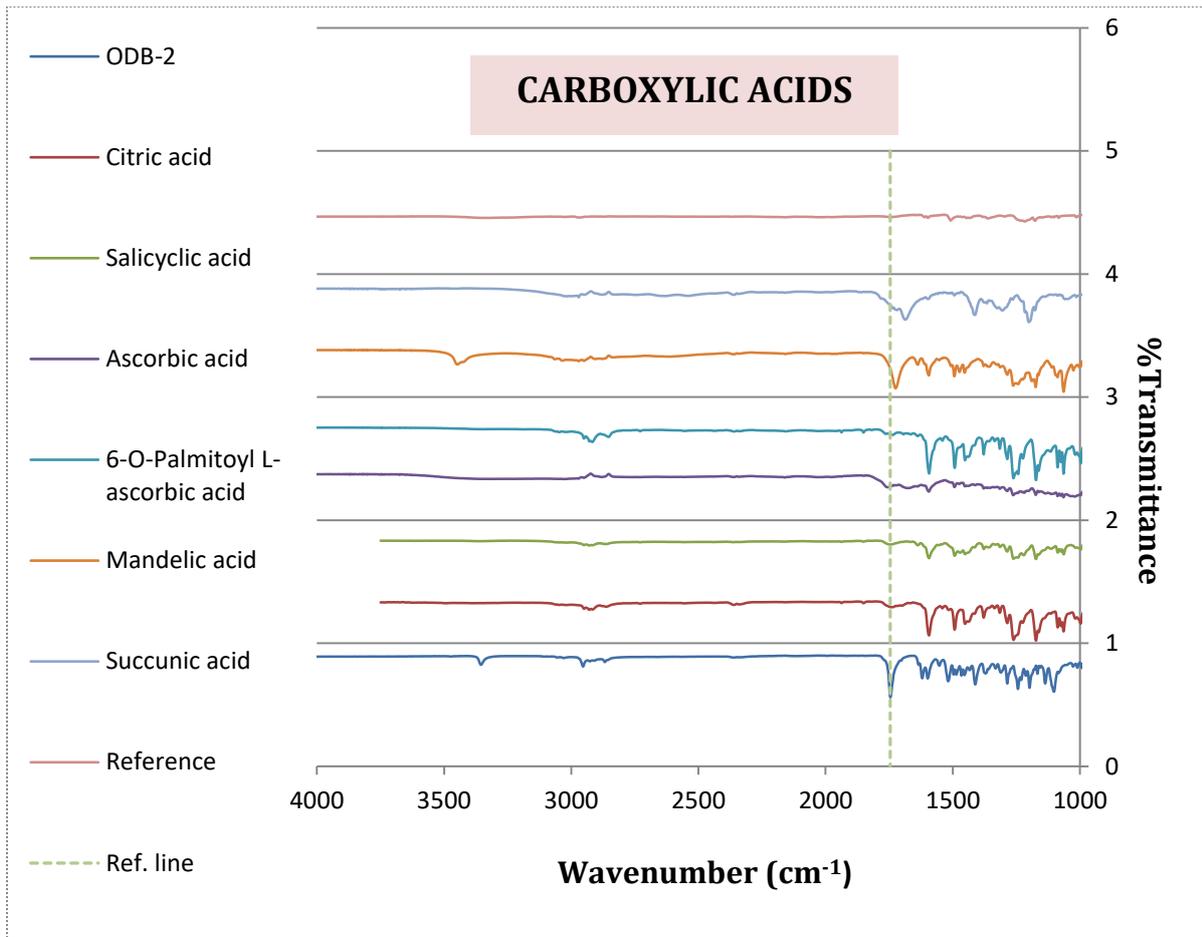
The reaction between a developer and leuco dye (ODB-2) is studied by monitoring the appearance, reduction or disappearance of the characteristic C=O stretching vibration peak in the FT-IR spectrum (Takahashi *et al.*, 2002). The intense C=O stretching band of the lactone ring ( $1754\text{cm}^{-1}$ ) decreases in all studied tannins, flavonoids and carboxylic acids. A complete disappearance of the C=O is observed in 6-O-palmitoyl L-ascorbic acid, ascorbic acid, salicylic acid and citric acid. This supports the results from the rapid screening. In fatty acids, a decrease in the C=O in the lactone ring band is observed with stearic acid and lauric acid but no change is observed with myristic acid. The C=O band remains unchanged in coumarin and sugar acids. Moreover, broad bands are formed with all sugar acids; mucic acid ( $1753\text{cm}^{-1}$ ), saccharic lactone ( $1710\text{cm}^{-1}$ ) and glucuronic acid ( $1786\text{cm}^{-1}$ ). These bands are still characteristics of lactone ring (Bellamy, 1975). A shift of the lactone must have occurred. A neat FT-IR spectra is obtained for glucose and sucrose with the reduction of the C=O ring. Similarly, to tannins, the C=O band decreases in all monomeric phenolic compounds and  $\beta$ -sitosterol except syringaldehyde. Resins – Abietic acid also gave a promising result in this regard.

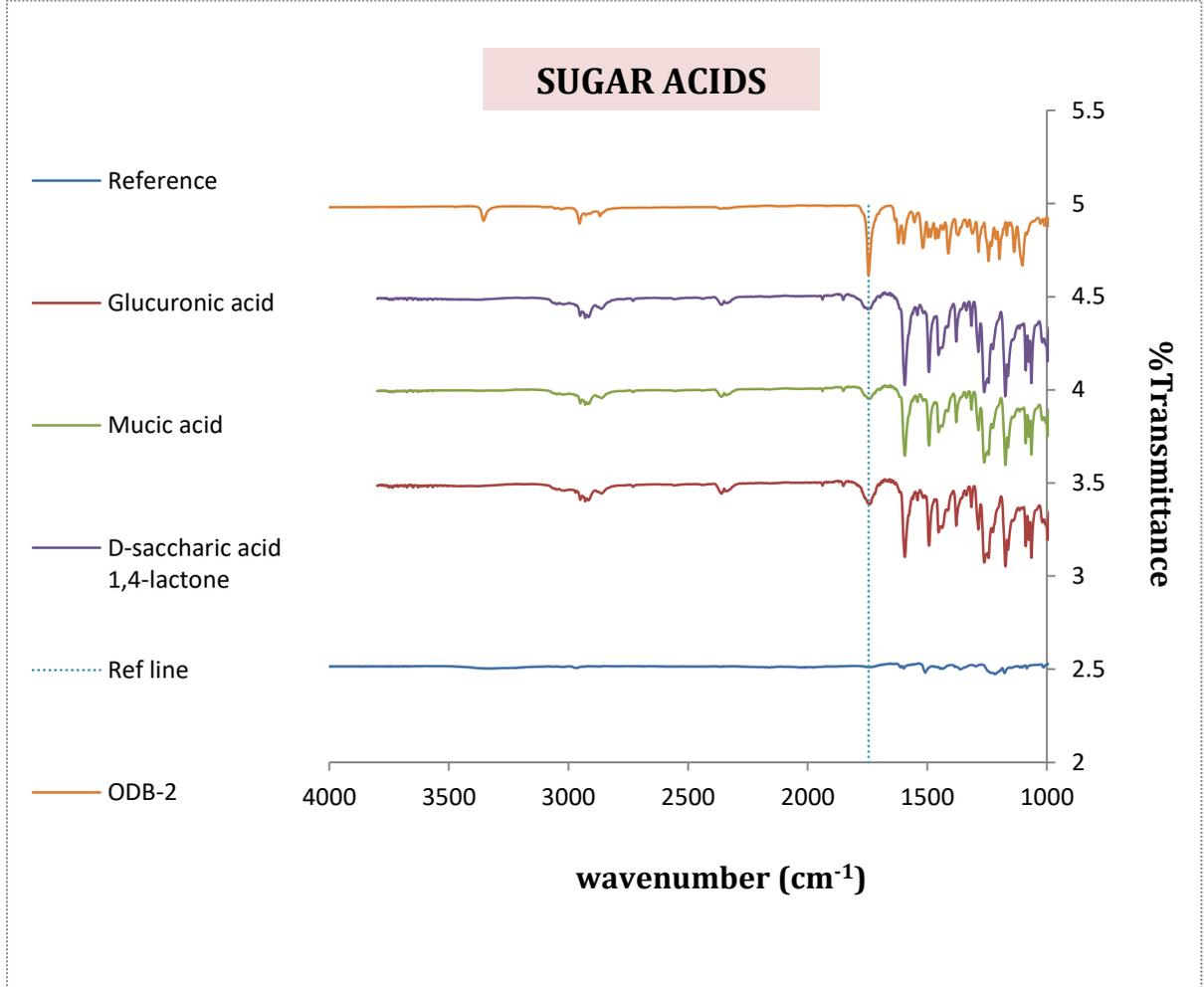
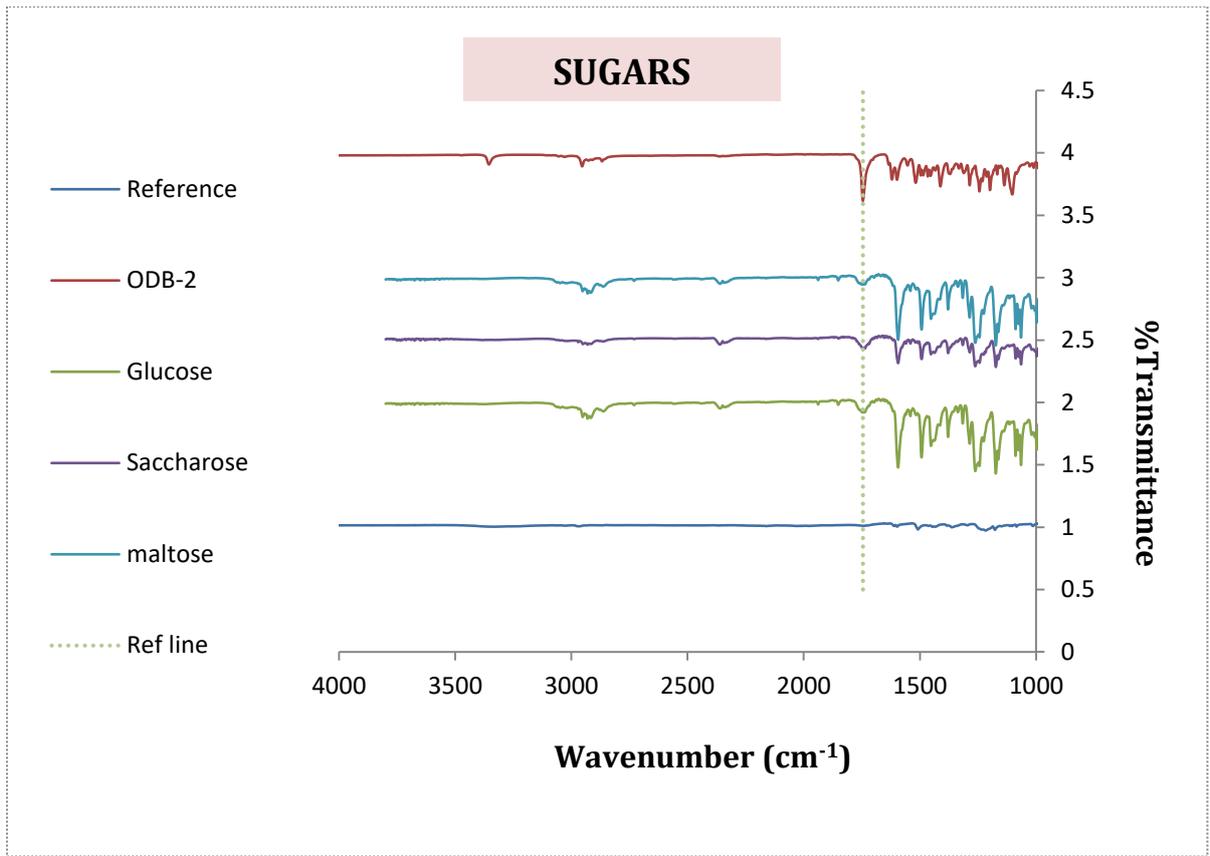
## FLAVONOIDS

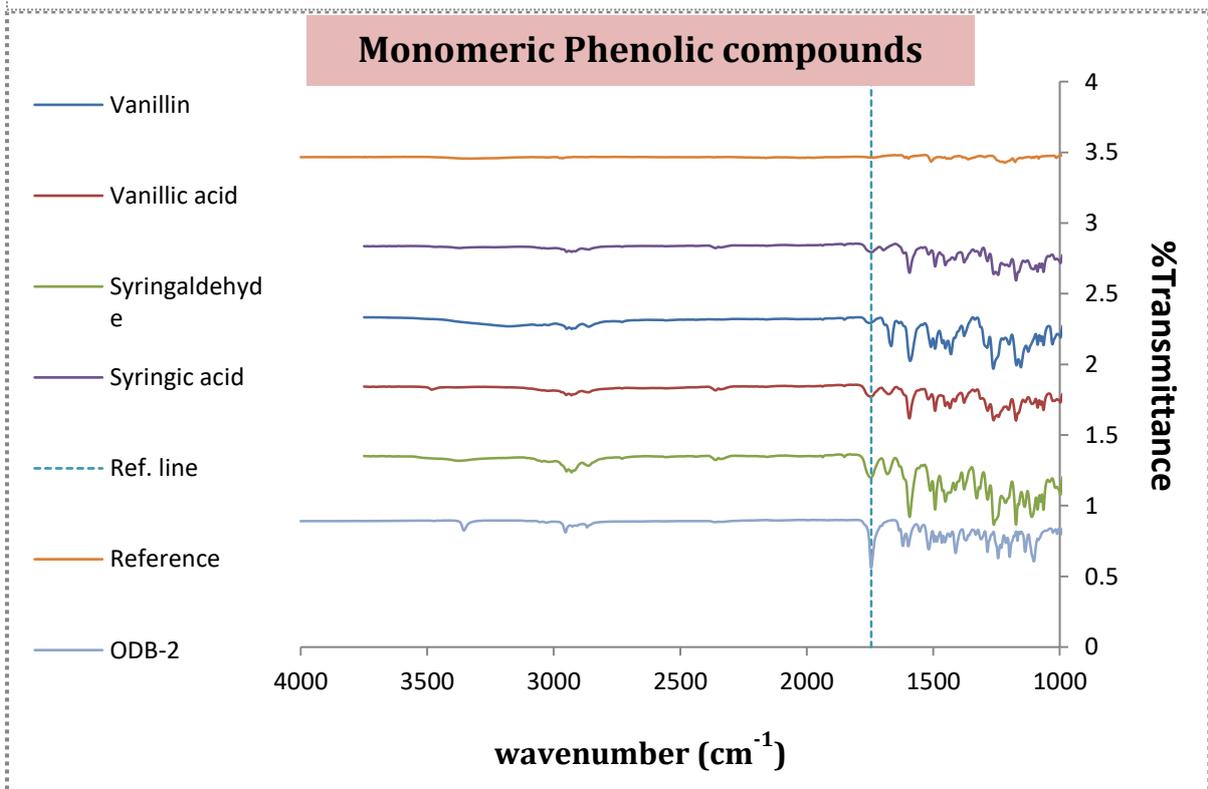
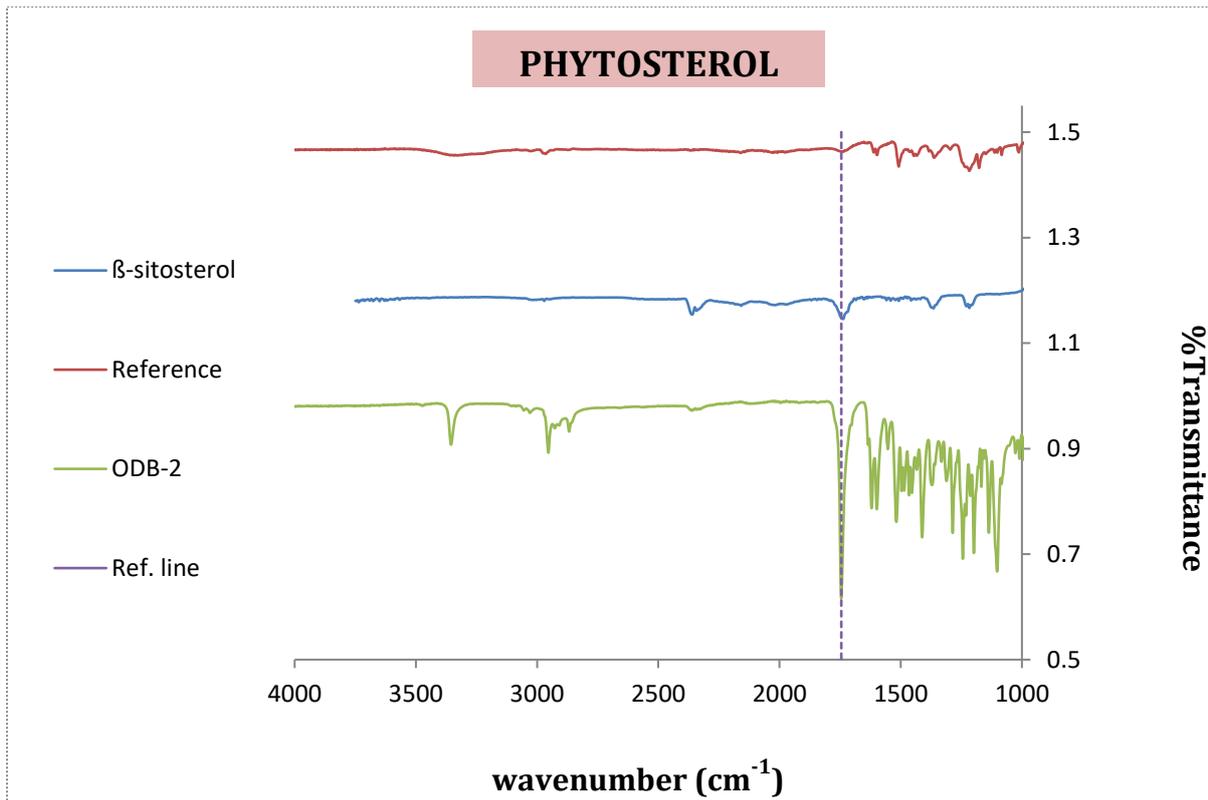


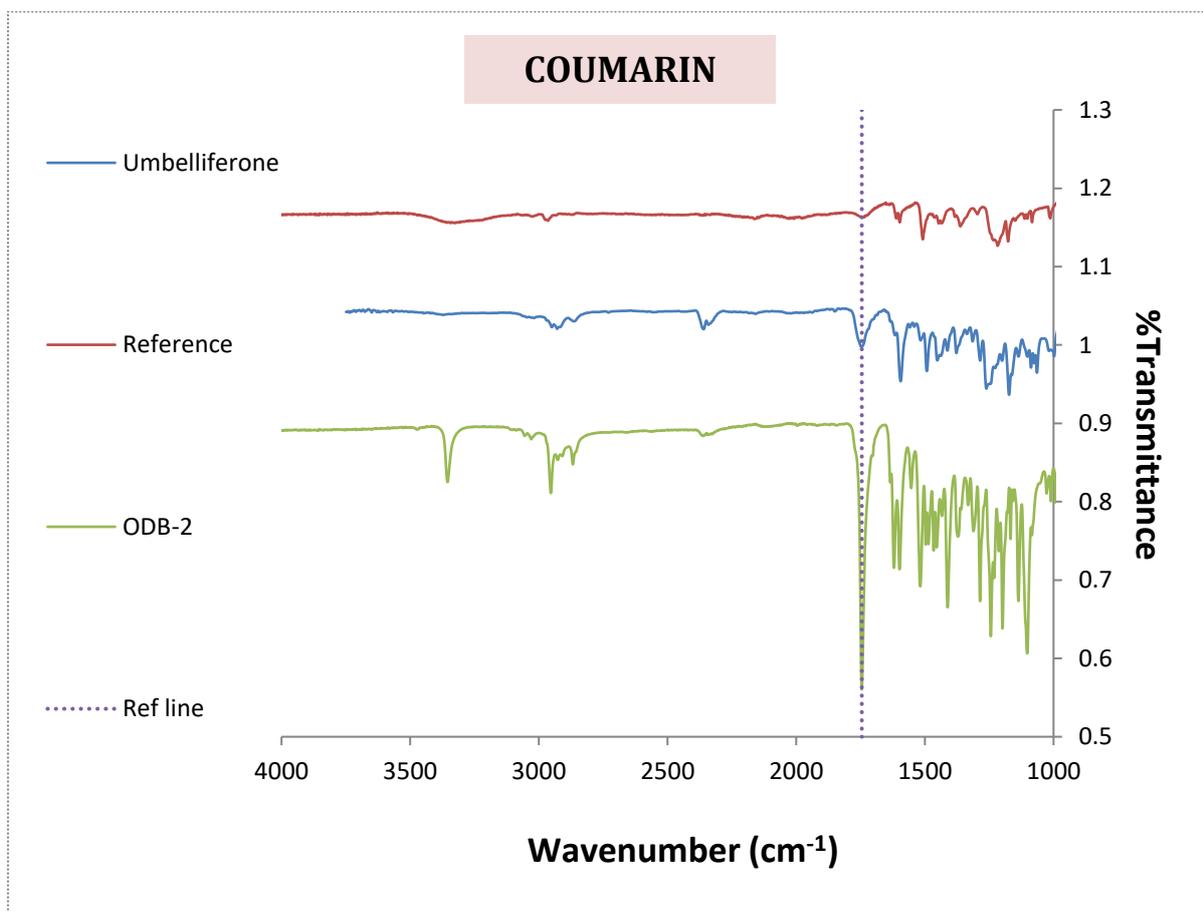
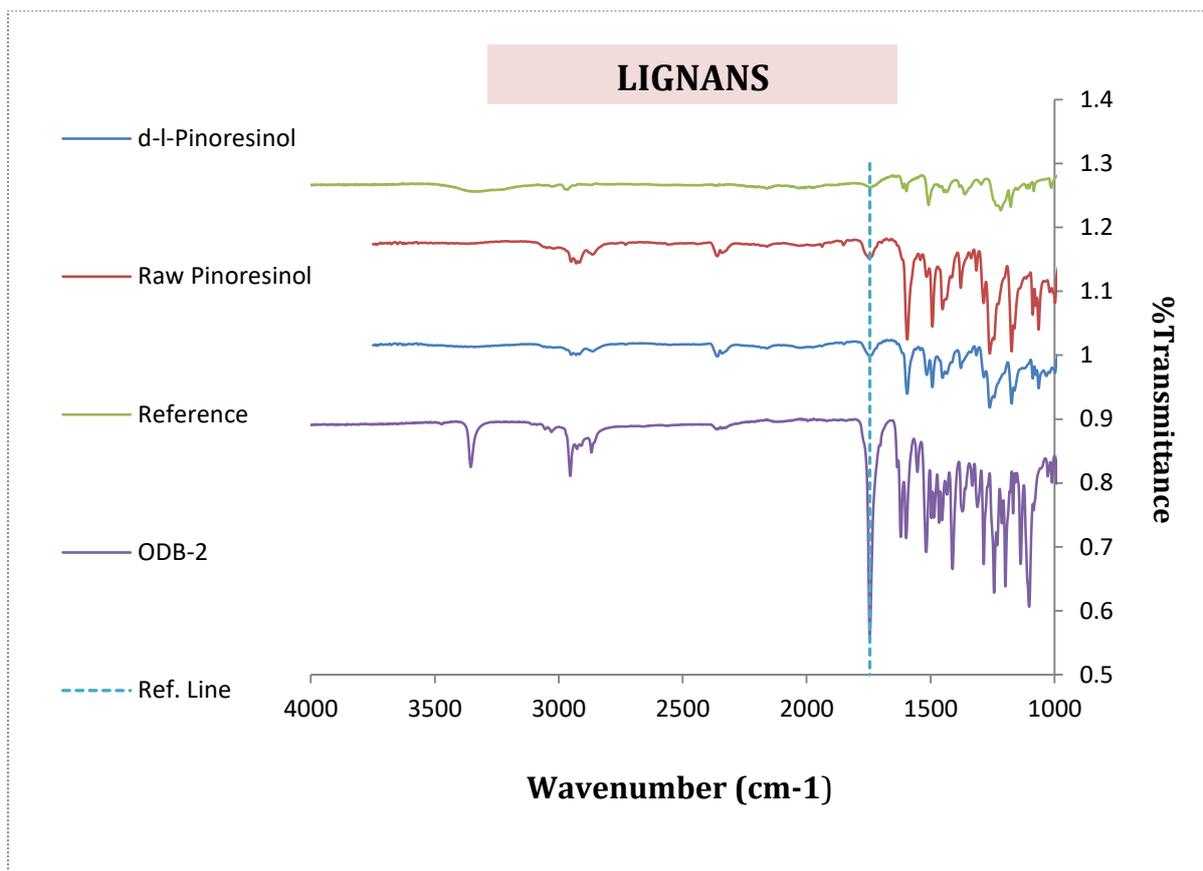
## TANNINS

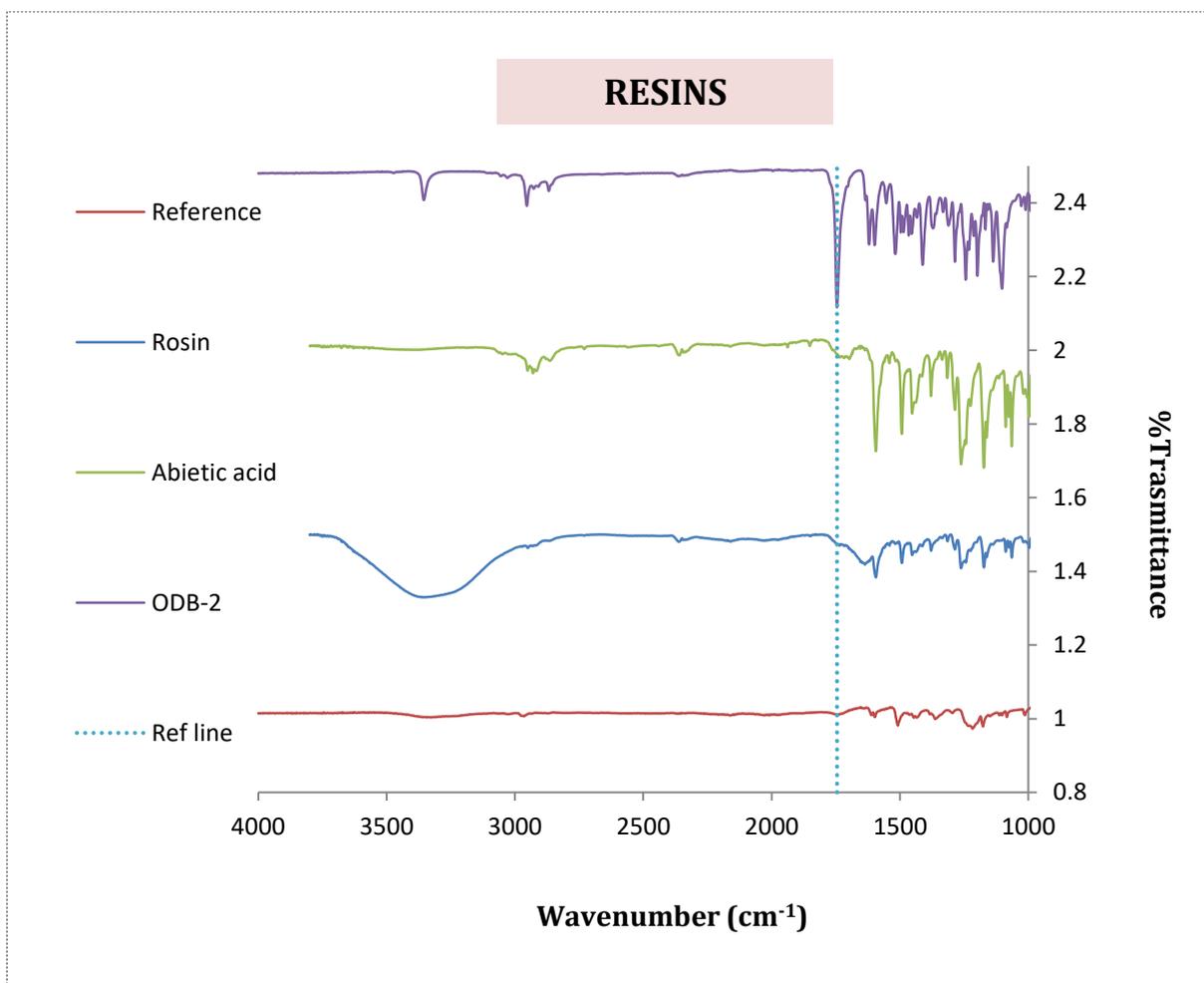
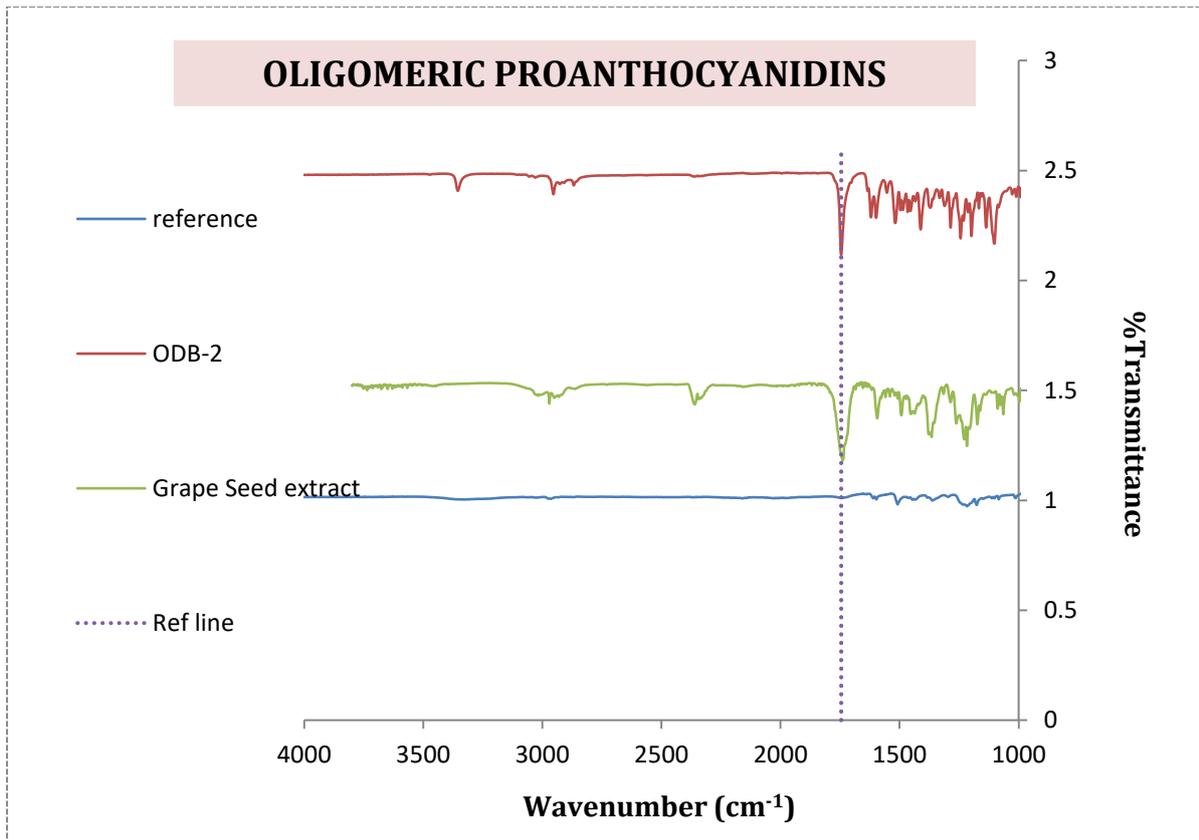












### **AP1.2.3. Ultraviolet and visible (UV-vis) spectrum analysis**

The UV analyses of the screened compounds were carried out with Perkin Elmer Lambda 650 UV/vis spectrometer as described by Hojo *et al.*, 2009 with little modification. 0.00532 g, 0.04mmol ODB-2 was dissolved in 20 ml acetonitrile to produce a colourless solution, 0.04 mmol of the screened substance was then added to produce black colour. For undissolved mixture, the supernatant was separated with a 0.25  $\mu$ m filter and obtained solution was used for the UV-vis absorption spectrum analysis. Results are shown in figure 8. Firstly, the colouring and decolouring characteristics of ODB-2 was investigated as described by Endo *et al.*, 1991. Five UV measurements were made and the results are shown in figure 9. As reported by Hojo *et al.*, 2009, fluoran dye exists as the colorless lactone form in acetonitrile. Addition of an electron acceptor in form of acid, or phenols produces black colour and absorption on the visible region. In this light, UV absorption spectral method was used to compare the coloring and decoloring reversible state of ODB-2 in acetonitrile and hydrochloric acid. The UV spectra of 0.01 mmol of ODB-2 in 30ml acetonitrile showed no absorption spectra. With the addition of increasing concentration of HCl, 0.01M, 0.02M and 0.03M, increased absorption spectra at 450nm and 590nm were observed. These bands which represents wavelengths of complementary colour, confirm the transformation of ODB-2 from the closed lactone ring form to the opened lactone ring form (Yanagita *et al.*, 2006) . Further, addition of 8ml 4M NaOH to the 0.01M mixture initiated a decolouration process. Higher quantity of the NaOH led to a complete decolourisation. This confirms that the colouration or decolouration of ODB-s depends on the acidity of its environment. UV absorption spectra of screened compounds were measured likewise. 1mg of dye-developer crystals were dissolved in acetonitrile in a 25 ml volumetric flask. Solutions with very high colour thickness were diluted with excess solvent and their absorbance values were corrected.

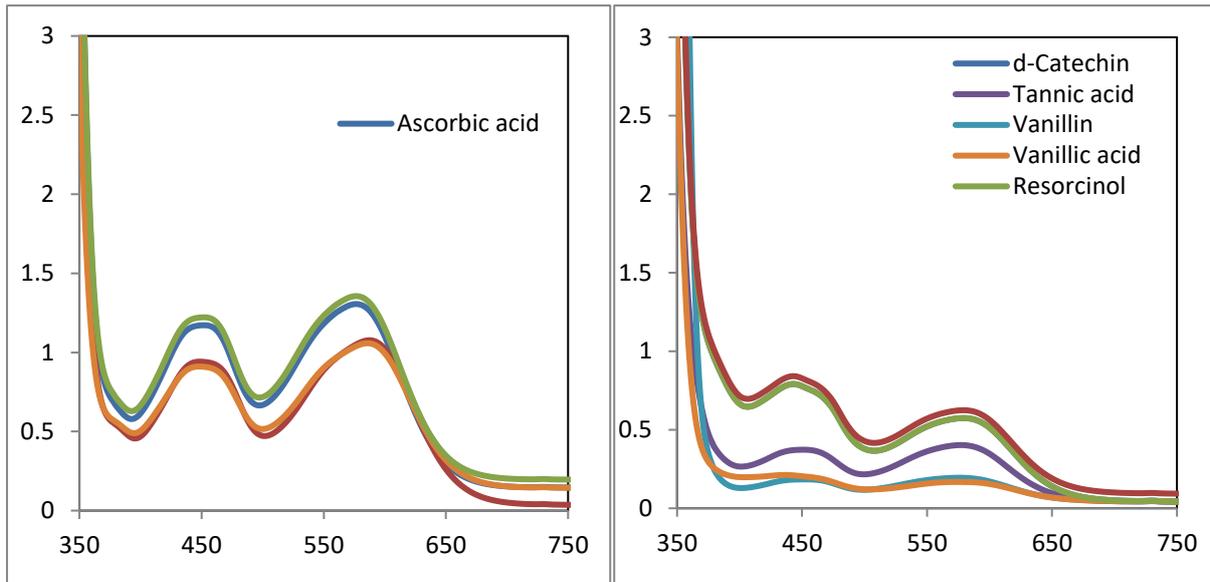


Figure 8. UV absorption spectra of ODB-2 + screened substances in acetonitrile

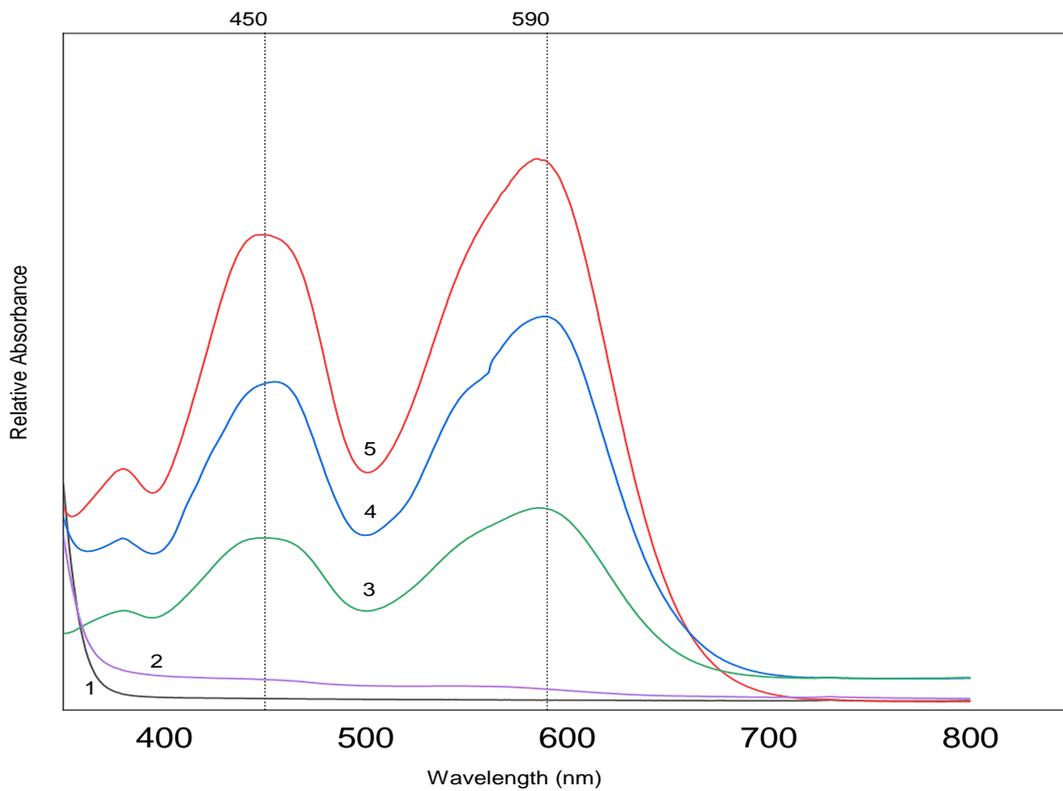


Figure 9. UV-visible absorption spectrum (pathlength of 1.0cm) of ODB-2 in acetonitrile (1); ODB-2 in acetonitrile + 0.01M HCL + 8ml 4M NaOH (2); with varying concentration of hydrochloric acid; ODB-2 in acetonitrile + 0.01M HCL (3) ODB-2 in acetonitrile + 0.02 M HCL (4); ODB-2 in acetonitrile + 0.03M HCL

## **AP2 Fractionation and purification**

To simplify the complex mixture of compounds investigated in AP1, several fractionation and purification techniques were carried out.

### **AP2.1 Fractionation of pulping liquor**

The focus of this section is to report the fractionation of pulping liquor. The aim is to separate the high molecular weight compounds from the low molecular weight compounds and further purify the low molecular weight compounds into individual compounds or less complex fraction. The colour developing potential of the compounds and fractions is then tested with our screening method (AP1). Some of the extracts obtained from this process have been tested and reported in AP1.

#### **AP2.1.1. Materials**

- Beech Liquor from Thünen Institute
- Organosolv Liquor
- Pine sulfate liquor
- Softwood liquor from Slovakian paper mill

#### **AP2.1.2. Characterization of black liquor**

The physicochemical properties of the black liquors as determined by standard laboratory methods are shown in figure 10. Solid content was determined using the evaporation method. About 50 ml of the liquor was pipetted into a pre-weighed aluminium evaporating dish. The dish and sample were weighed and then dried in a drying oven at 105°C overnight. After drying, the dish was cooled in a desiccator in the presence of P<sub>2</sub>O<sub>5</sub>. The total solid content was calculated as the difference between the initial and final weight of sample reported as percentage of the initial weight. The determination is done in replicate and average solid content was reported.

For ash content determination, the solid obtained from the solid content determination was transferred into a muffle furnace and heated at about 700°C until no trace of blackness was observed. Ash content is also reported in percentage.

**AP2.1.3. Isolation/Precipitation of high molecular weight lignin****• Organosolv Liquor**

One (1) litre of organosolv liquor was mixed with 2 litres deionized water. The deionized water was slowly added to the waste liquor and carefully mixed. The mixture was then placed in an ultrasonic bath for one hour. The precipitate produced was allowed to stand overnight in the refrigerator. Produced lye was filtered through a filter over a porcelain funnel and a suction bottle assisted with a water jet pump. Paper filters of the brand LLG Lab ware with a diameter of 150 mm and a pore diameter of 12-25  $\mu\text{m}$  were used. The filtrate was separated and residue was washed with 1.5 l of 40 °C warm deionized water. The container used for precipitation was also washed to recover all residues. The residue was pre-dried overnight at 40 °C in the circulating air drying cabinet on the filter and the porcelain chute. The residue was then scratched off the filter and dried in a porcelain dish for 24 hours above Phosphorus Pentoxide  $\text{P}_4\text{O}_{10}$  at room temperature in a vacuum drying oven. The weight of residue (lignin) was determined gravimetrically.

**• Beech/Pine sulfate/Softwood Liquor**

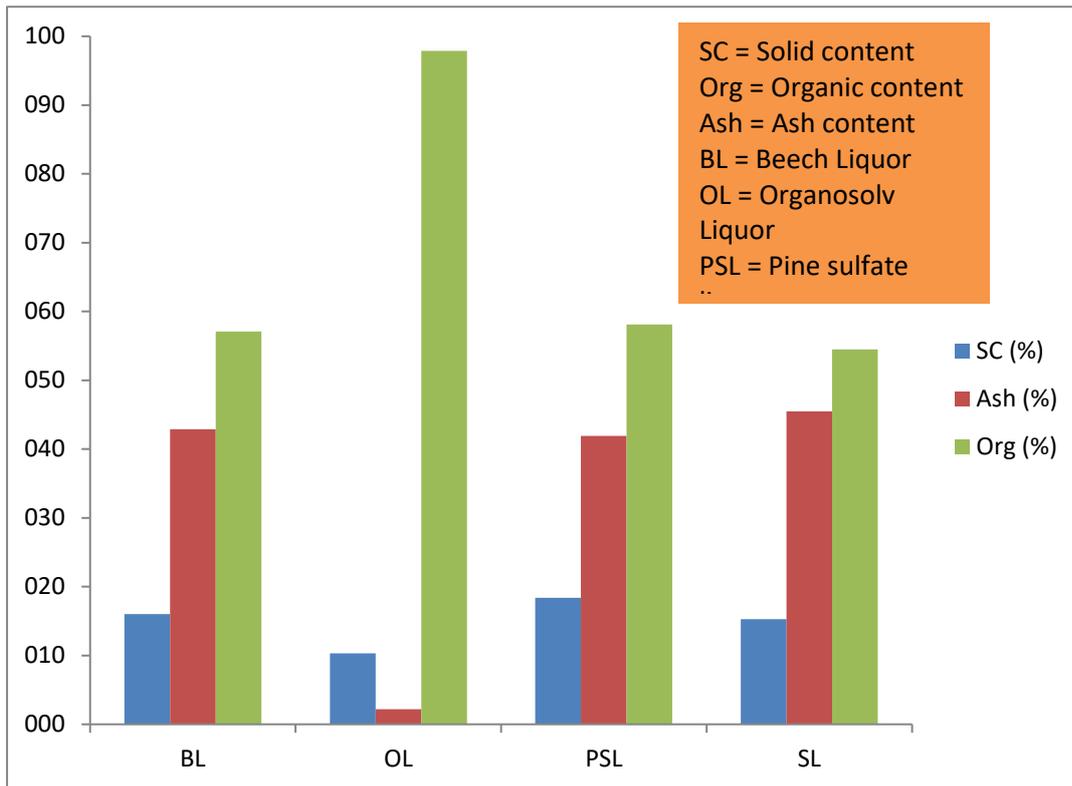
To precipitate the high molecular weight lignin from beech/pine sulfate/softwood liquor, acid precipitation method was utilized.

2 Litre (L) liquor was acidified to pH 10.07 by dropwise addition of 500ml of 0.1M  $\text{H}_2\text{SO}_4$ . Further acidification to pH 3.05 was achieved by the addition of 1M  $\text{H}_2\text{SO}_4$  at 80°C. The mixture was allowed to stand overnight and thereafter centrifuged at 4000 rpm for 45 mins. Part of the filtrate was decanted and the rest was withdrawn through filtration under vacuum. The residue (lignin) was washed with warm water (40°C) to neutral pH and dried in a drying oven at 50°C. The supernatant and washing liquid (filtrate) were combined, mixed and stored in the cold room for further treatment.

**AP2.1.4. Liquid-Liquid Extraction of filtrate**

Extraction of filtrate to isolate the hydrophobic component was achieved using MTBE as a solvent in a continuous liquid-liquid apparatus (Fig 8). In this technique, the solvent was continuously heated in a water bath. The steam rose by an upwardly inclined elbow into the apparatus. With the help of a condenser, the gaseous solvent was condensed and led in a funnel-shaped glass diffusion tube with a fritted-like base which acts as a diffusion path to carry solvent all through the filtrate medium. Thereby the hydrophobic components were transferred to the top of the solution. Solvent flows with the desired extract into the flask. The

extraction was done with 1000 ml filtrate and a total of 500 ml MTBE for 18hours. After extraction, the extract was filtered to remove suspended substances using a filter paper (fig 9). The clear extract was then dried with the addition of 10 g magnesium sulphate. Filtration was repeated again to remove the used magnesium sulphate. Extract was thereafter subjected to distillation under vacuum with a rotary evaporator to remove the residual solvents (fig 10). The dried extract was weighed and stored for further processing.



**Fig 10. Physicochemical characteristics of studied pulping liquor**



**Fig 11. Sample of pulping liquor**



**Fig 12. Acid precipitation of Lignin**



**Fig 13. Lignin sample**



**Fig 14. Continuous Liquid-Liquid Extraction of filtrate**



**Fig 15. Filtration of Extract**



**Fig 16. Distillation of extract using rotary evaporation**



**Fig 17. Dried extract**

**Table 2: Yield of high molecular weight and extract from pulping liquor**

<b>Pulping liquor</b>	<b>Lignin (%)</b>	<b>Extract (%)</b>
Beech organosoly liquor	26.7	11.7
Beech sulfate liquor	20.0	11.6
Pine sulfate liquor	31.9	5.8
Softwood liquor	29.1	12.3

**\*Values are based on the solid content of the samples**

**AP2.1.5. Screening of Extracts**

The rapid screening of extracts was done using our developed method. The result is reported under AP1.

**AP2.1.6. Fractional Vacuum Distillation of Extract**

Due to the complex nature of the extract as observed through our Gas Chromatography analysis (Figure 18 & Table 3), it becomes expedient to further fractionate the extract. Fractional vacuum distillation was attempted. The distillation set-up consists of a vacuum pump, cowhead adapter, six distilling receivers, a fractionating column connected to a water condenser (at room temperature), a round bottom flask containing the extract placed on an oil bath heated by a heating mantle (Figure 19).

About 10 g of beech extract was used in a pre-weighed round bottom flask. The oil bath was heated to a maximum temperature of 200°C and the pressure of the system was gradually reduced to the lowest pressure possible. The temperature of the distillates was monitored with a thermometer. In total, 7 fractions were collected in the distilling receivers and heavy dark residue remains in the flask (Figure 20). The temperature range of fractions and other operating parameters are as shown in table 3

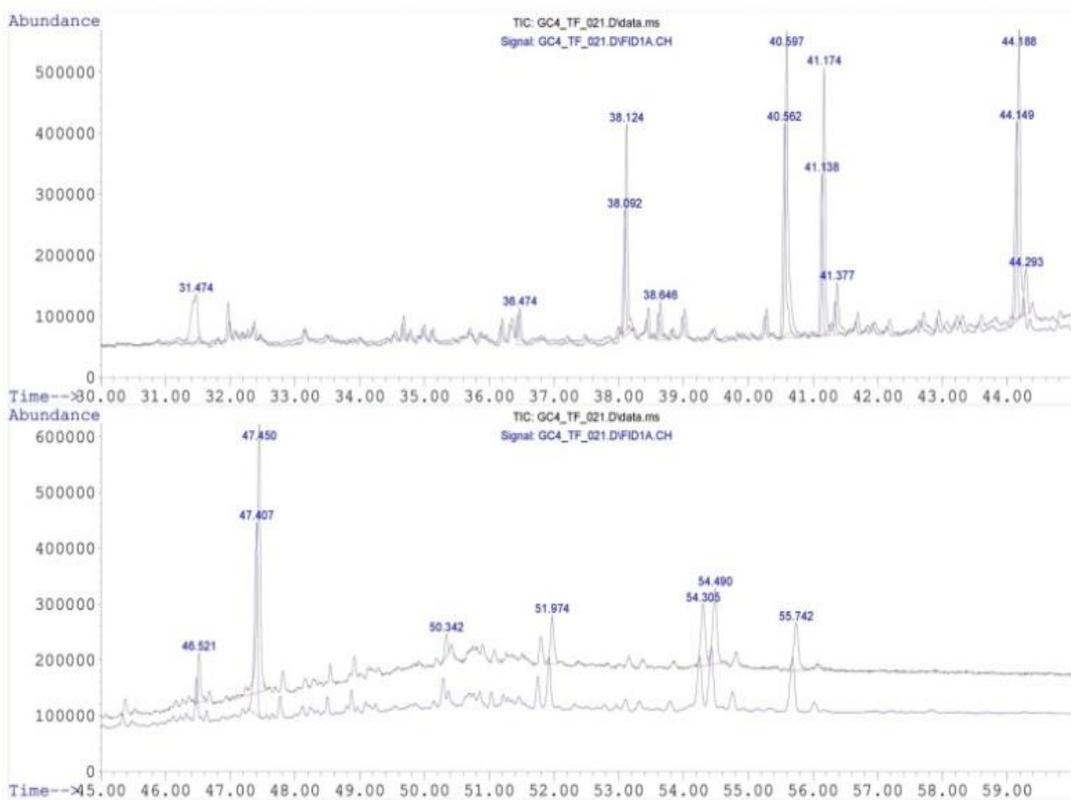
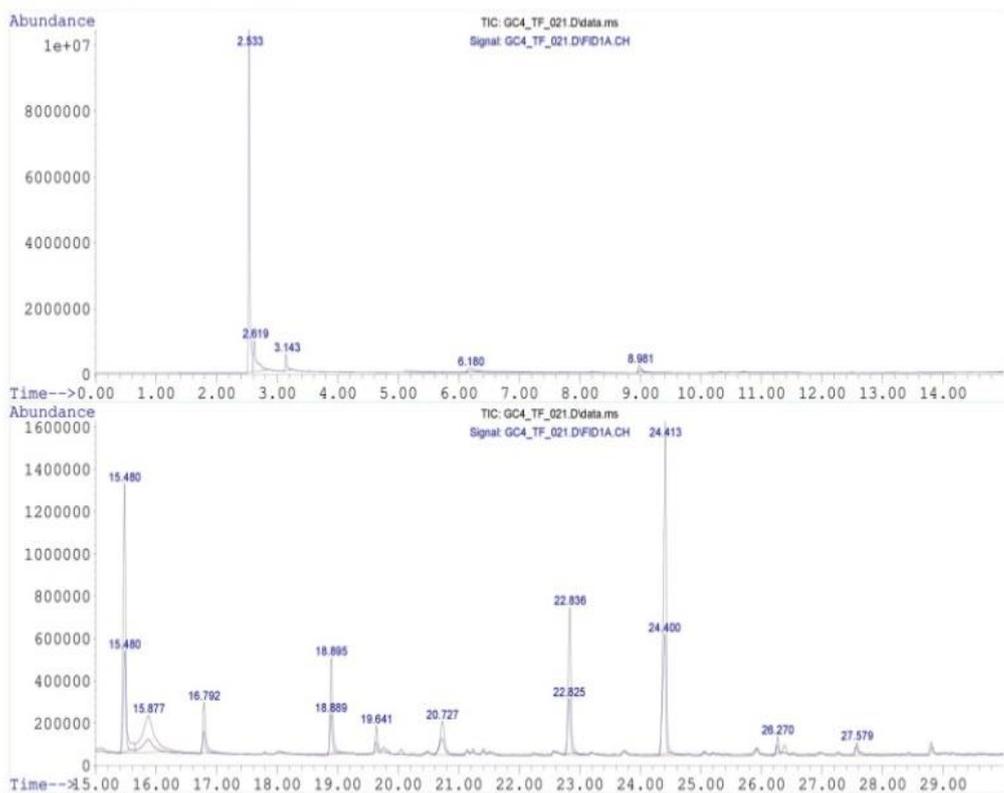


Fig 18: Py-GC/MS of beech extract shows that it is enriched in low molecular weight phenols. These phenolic compounds are lignin fragments with potential to act as developer due to the OH groups which are readily available for a proton-transfer reaction.

**Table 3: Overview of compounds detected in the MTBE Extract of Beech Liquor**

Peak Nr	Retention time (min)	Compound name	Qual.
#	min		
1	6.18	3-Pentanol	50
2	8.981	Guaiacol	94
3	15.48	Syringol	97
4	15.877	Syringol	97
5	16.792	Vanillin	87
6	18.895	Acetoguaiacone	90
7	19.641	4-Ethyl syringol	94
8	20.727	4-Vinyl syringol	97
9	22.836	Syringaaldehyde	98
10	24.413	Acetosyringone	94
11	26.27	Propiosyringone	58
12	27.579	Dihydrosinapylalcohol	95
13	31.474	cyclic octaatomic sulfur	94
14	36.474	2-oxo-6-phenyl-4-(2-hydroxyphenyl)-1,2-dihydropyrimidine	53
15	38.124	tris(2-methylphenyl)-Phosphine	86
16	38.646	?	
17	40.597	?	
18	41.174	?	
19	41.377	4,4-methylenebis (2,6-dimethoxy) Phenol	95
20	44.188		
21	44.293		
22	46.521	Methyl (3,4,6,7-tetramethoxy - 1-phenantryl) acetat	83
23	47.45	?	
24	50.342	?	
25	51.974	?	
26	54.305	?	
27	54.49	?	
28	55.742	?	



**Figure 19: Fractional vacuum distillation set up**



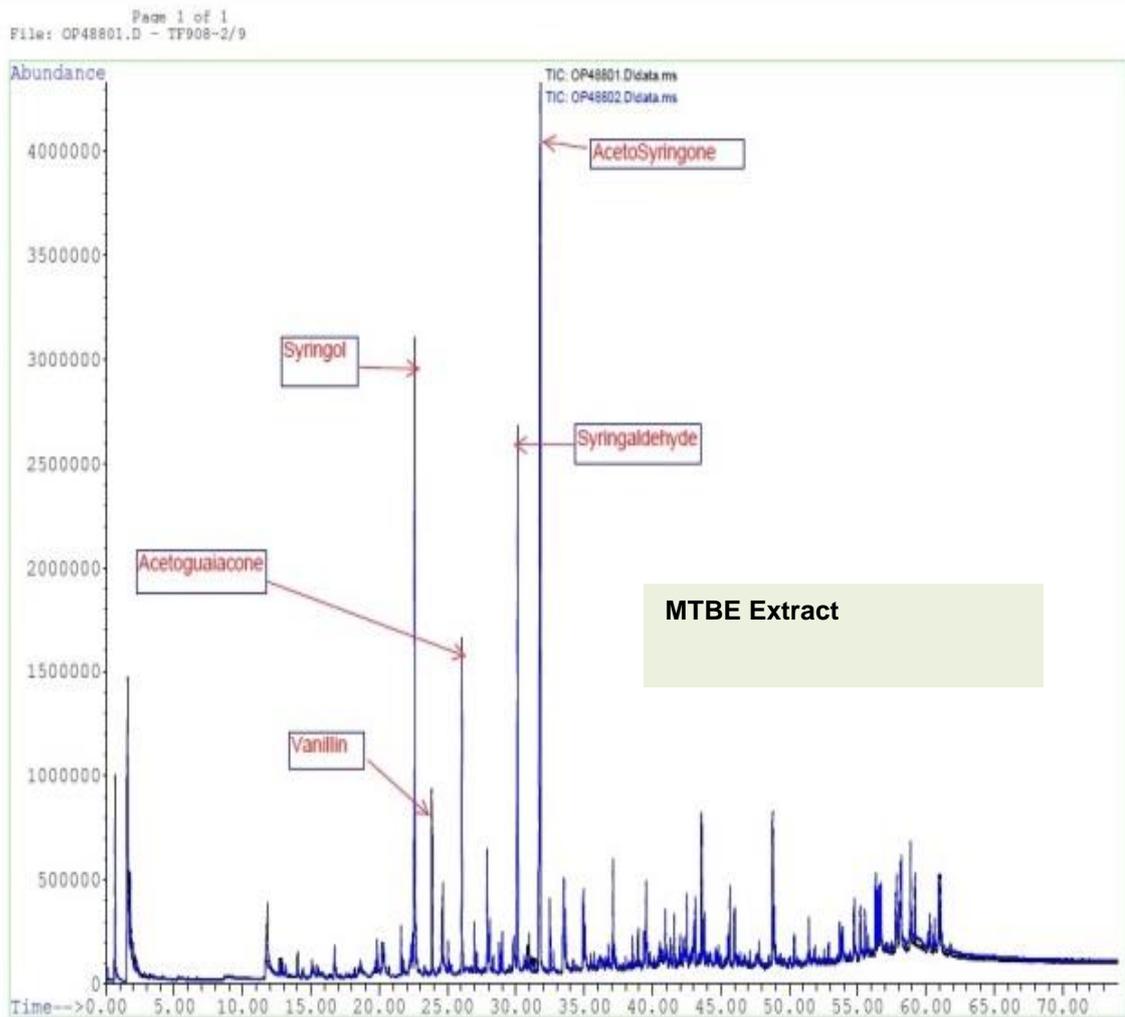
**Figure 20: Heavy black residue after fractional vacuum distillation.**

**Table 4: Boiling point range of fractions**

S/N	Boiling point range (°C)	Oil bath temperature (°C)	Pump Pressure (mbar)
1	75-80	120-125	250
2	85-96	120 -125	30
3	96-100	160-170	30
4	100-110	170-175	5
5	110-122	175-180	5
6	120-145	185	0
7	80	200	0

**AP2.1.7. Py-GC/MS analysis of distillate fractions.**

The distillate fractions, residue and main extract were analysed using the Py-GC/MS method. The pyrolysis system used is a Double-Shot pyrolyzer PY-2020iD with auto- Shem autosampler (Autosampler) AS-1020 E from Frontier Lab. Results of Py-GC/MS analysis shows that the main extract and fractions are composed of monomeric phenols and derivatives such as syringol, syringaldehyde, vanillin, acetoguaiacone, acetosyringone etc. These compounds are however present as a mixture.



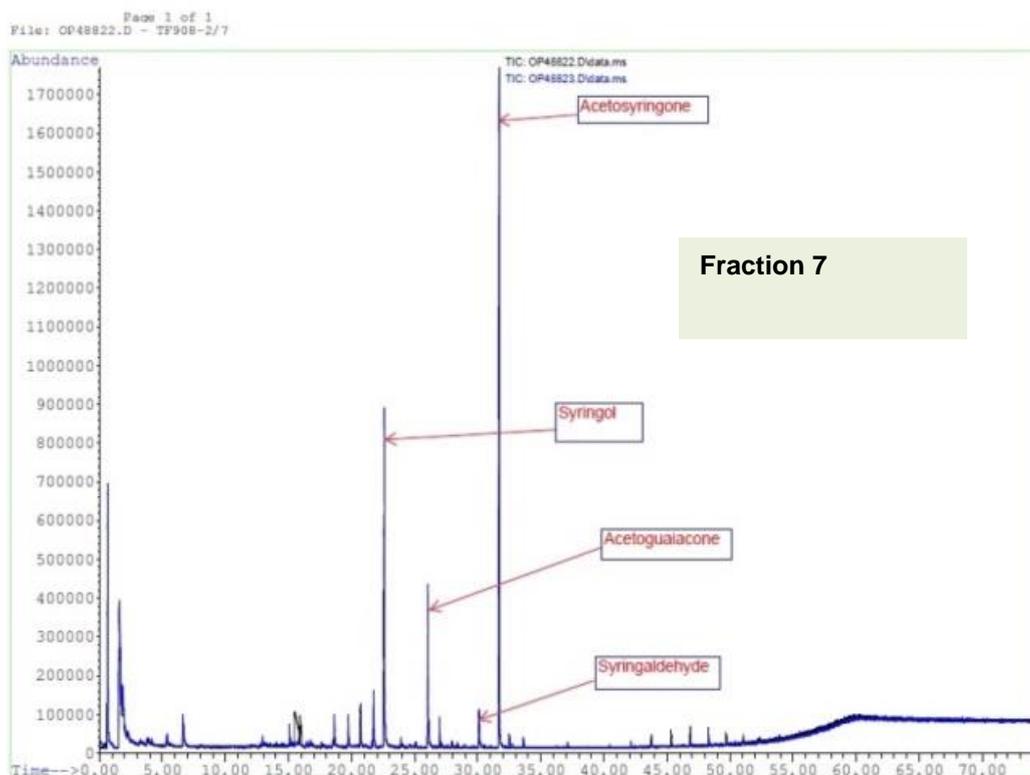
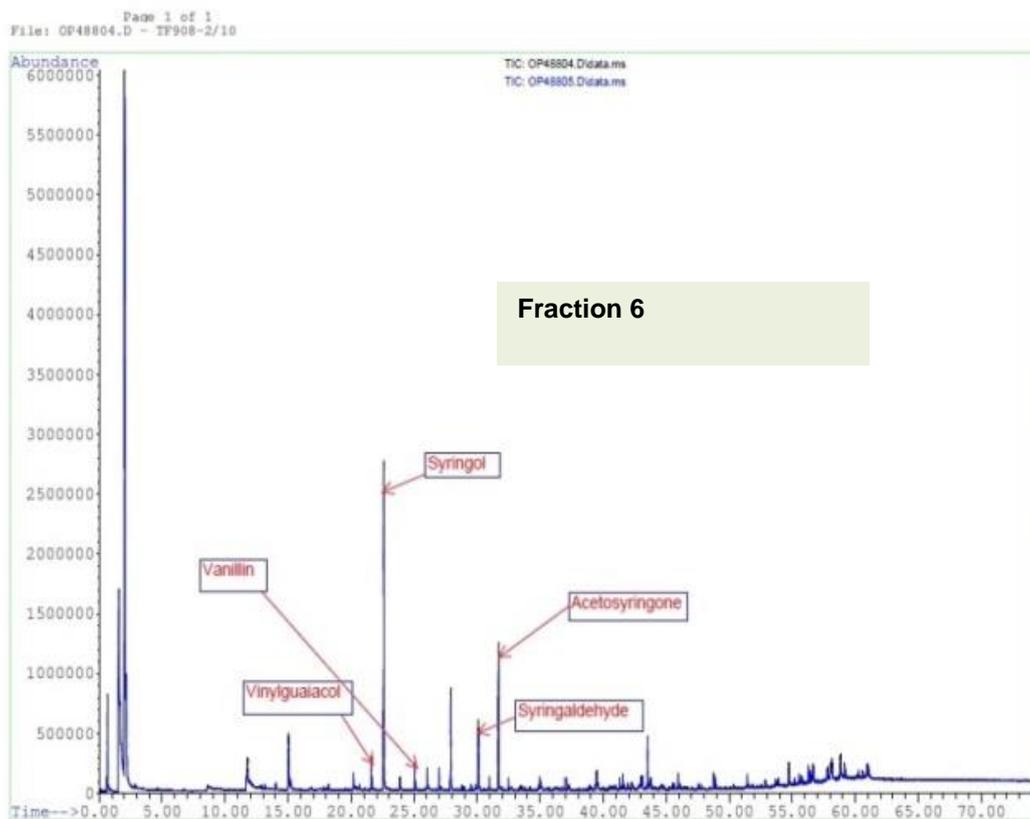


Fig 15: Py-GC/MS chromatogram of fractions from fractional vacuum distillation. (a) MTBE Extract; (B) Fraction 6 (c) Fraction 7

**AP2.1.8. Screening of distillates**

Fractions obtained from the vacuum distillation were tested for their colour-developing potential by mixing with leuco dye. Due to the viscous nature of the distillates, it was difficult to get them into the capillary tube as explained in AP1. The samples only lined the wall of the capillary tube and this does not allow the much needed mixing with the colouring agent. Therefore, for the screening, the distillate was mixed with the colouring agent in an aluminium pan. Upon mixing, all the extracts gave a black colouration without the application of heat (Figure 21). This shows that the fractions contain compounds with high potential to act as colour developer. The developed colour solidified at room temperature and remained unchanged all through the period of analysis.

### AP2.1.9. Acid-base fractionation of extract

Acid base fractionation of extract of SL was carried out in order to separate the component of the extract into phenolics and neutral portion. This method is expected to produce more simplified fractions. Fractionation was done at 5 different pH: 12.30, 11.66, 10.32, 9.45 and 5.70. The procedure for fractionation is highlighted in the chart (Figure 22).

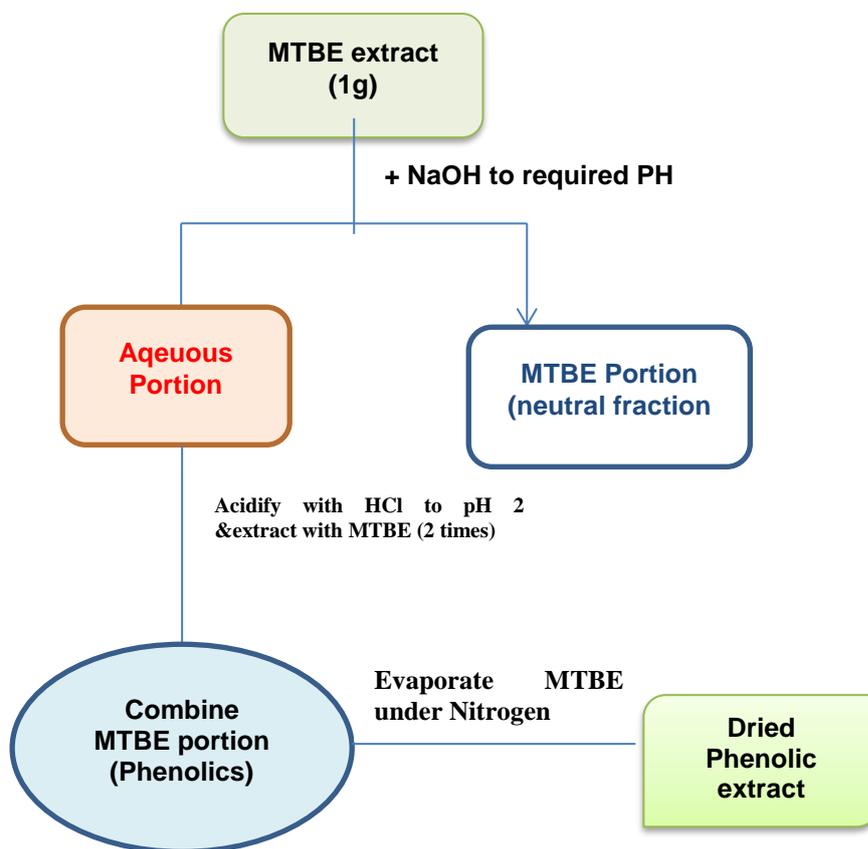


Fig 22: Procedure for the acid-base fractionation of extract from softwood liquor

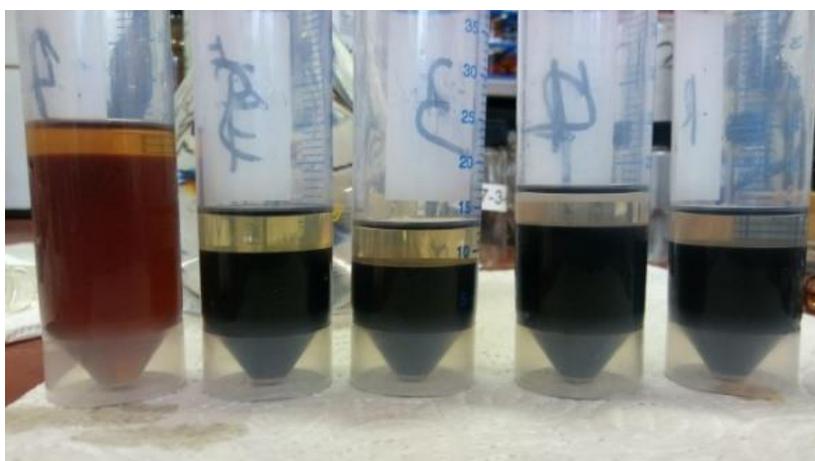


Fig 23: Basified extract at different PH.  
PH from Left: 5.7, 9.45, 10.32, 11.66, 12.30

**Table 5:**

<b>pH</b>	<b>Yield of acid-base extraction</b>	
	<b>Neutral (g)</b>	<b>Phenolic (g)</b>
<b>5.70</b>	<b>0.04035</b>	<b>0.1667</b>
<b>9.45</b>	<b>0.00021</b>	<b>0.33271</b>
<b>10.32</b>	<b>0.0006</b>	<b>0.1748</b>
<b>11.66</b>	<b>0.7279</b>	<b>0.43205</b>
<b>12.30</b>	<b>0.0022</b>	<b>0.4123</b>

The yield of the neutral and phenol portions of the extracts (based on the gram weight of the extract) is as shown in table 5. The difference between the sum of the Neutral and phenolic fractions and the initial weight is attributed to waste and left overs in the final aqueous portion. Multiple extractions may be necessary to achieve higher yield.

#### **AP2.1.10. Solid phase extraction of extract**

Solid phase extraction of extract from Beech liquor was previously attempted with PA & HR-X cartridge as the solid phase. The yield of fractions obtained was considerably low. Varian Bond Elut C18 was thereafter tested and improved results were obtained. Solid phase extraction was carried out using the method of Ruiz-Gutierrez and Perez-Camino (2000).

The separation was carried out under vacuum to circumvent the very slow process experienced when carried out without vacuum. The vacuum was carefully adjusted using a water jet pump to avoid interaction between sample, stationary and mobile phase.

The cartridge was conditioned with 5ml 100% distilled water. 500 $\mu$ L (~ 5mg) sample was completely drawn into the stationary phase.

Eight (8) fractions were collected in a pre-weighed sample tube using different solvent combinations as mobile phase. Sample code in bracket

1. Methanol / aq. dest (20+80) v/v (TF908-4-1)
2. Methanol/ aq. dest (25+75) v/v (TF908-4-2)
3. Methanol / aq. dest (30+70) v/v (TF908-4-3)
4. Methanol/ aq. dest (45+55) v/v (TF908-4-4)
5. Methanol / aq. dest (60+40) v/v (TF908-4-5)

6. Methanol/ aq. dest (80+20) v/v (TF908-4-6)
7. Methanol (100 %) (TF908-4-7)
8. Chloroform / Methanol (50+50) v/v (TF908-4-8)

The fractions were dried in a vacuum oven. The total weight of the fractions was 7.36mg (Table 6). This excess weight shows that the fractions were not totally dried. The weights were thereafter corrected.

**Table 6: Weight (mg) of fractions from SPE**

Sample code	Weight/ mg
TF908-4-1	1,63
TF908-4-2	0,63
TF908-4-3	0,71
TF908-4-4	1,01
TF908-4-5	1,05
TF908-4-6	1,29
TF908-4-7	0,62
TF908-4-8	0,42

#### **AP2.1.11. Gel permeation chromatography (GPC)**

To further test the possible fractionation of extract, GPC was carried out using Sephadex LH 20 with a glass column (Econo Column, 2.5x 50 cm) and ammonium chloride buffer.

To prepare the mobile phase, in a 2 L beaker, 54 g ammonium chloride was dissolved in 250 ml pure bi-distilled water. 350 ml ammonia solution was added and then made up to 1 L with pure bi-distilled water. The pH of the buffer solution was 10. The collected pools were dried by rotation evaporation then transferred with water in a 30 ml screw vial and extracted with MTBE. The MTBE-phase was dried under nitrogen. From the results of the thermal desorption--GC/MS carried out, it was observed that the buffer is incompatible with the chromatography system; hence a new solid phase was attempted.

In the new method, Sephadex G10 was employed as the mobile phase without the ammonium buffer (Hellsten *et al.*, 2013). The same glass column was utilized. Under 6 hours, 60

fractions were collected (figure 24) and pooled into seven (table 7 & 8). The collected pools were dried by rotation evaporation then transferred with distilled water into a 4 ml screw vial. Afterwards, the samples were dried in a vacuum oven at 50°C over the weekend. Samples were dissolved in  $\text{CHCl}_3$  and prepared for Thermal Desorption-GC-MS measurements.

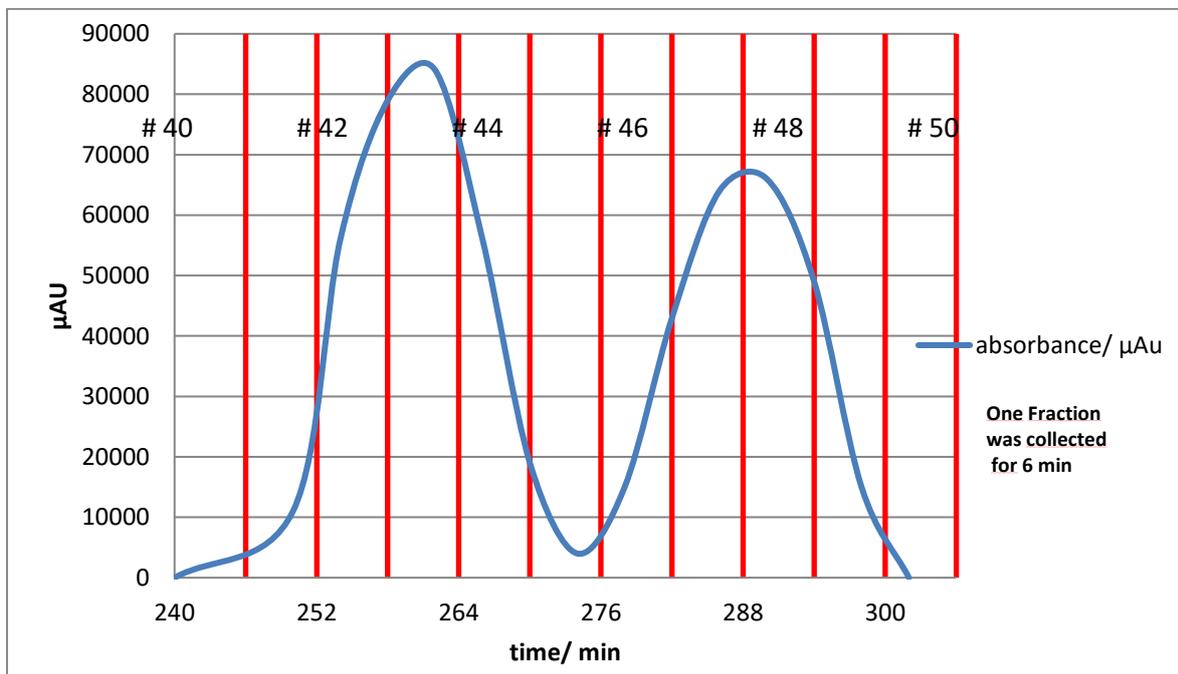
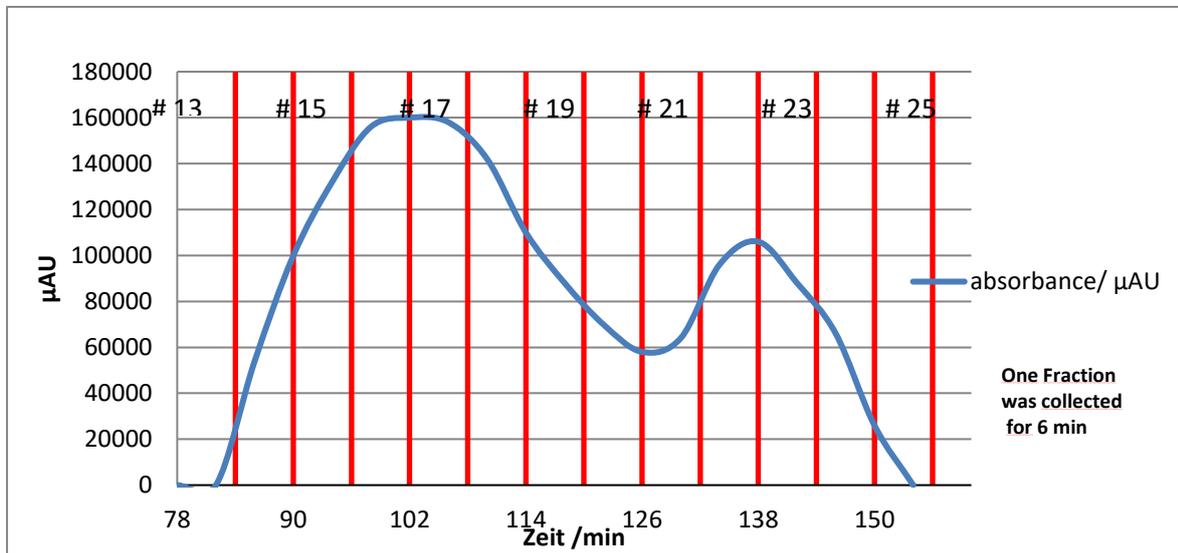


Fig 24: Chromatogram from GPC fractionation of extract using Sephadex LH 20

**Table 7: Pool of Fractions from GPC fractionation of extract using Sephadex LH 20**

<b>Pool</b>	<b>Fractions</b>
1	# 13 - 18
2	# 19 - 21
3	# 22 - 25
4	# 40 - 44
5	# 45
6	# 46 - 50

**Table 8: Pool of Fractions from GPC fractionation of extract using Sephadex G10**

<b>Pool</b>	<b>Fractions</b>	<b>Weight (mg)</b>
1	# 15 - 18	1.1
2	# 19 - 21	7.4
3	# 22/23	2.6
4	# 24 - 26	4.1
5	# 27 - 30	0.5
6	# 33 - 41	0.3
7	# 45 - 60	0.6

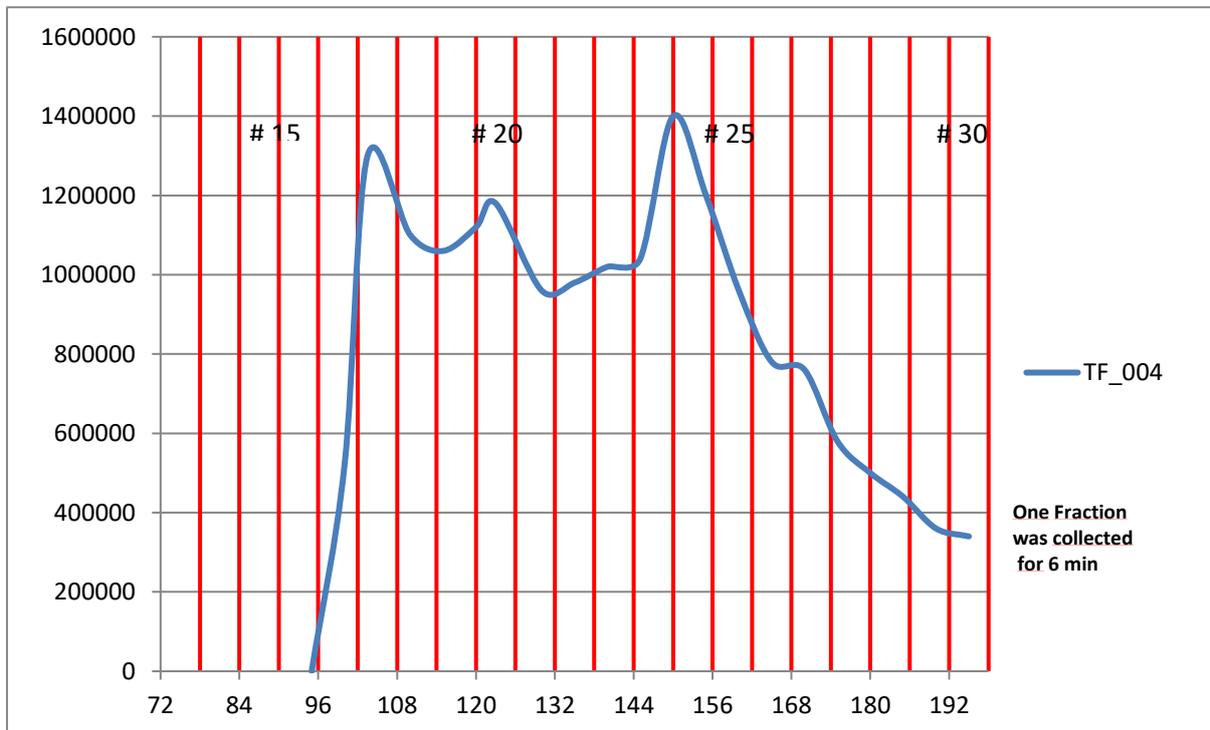
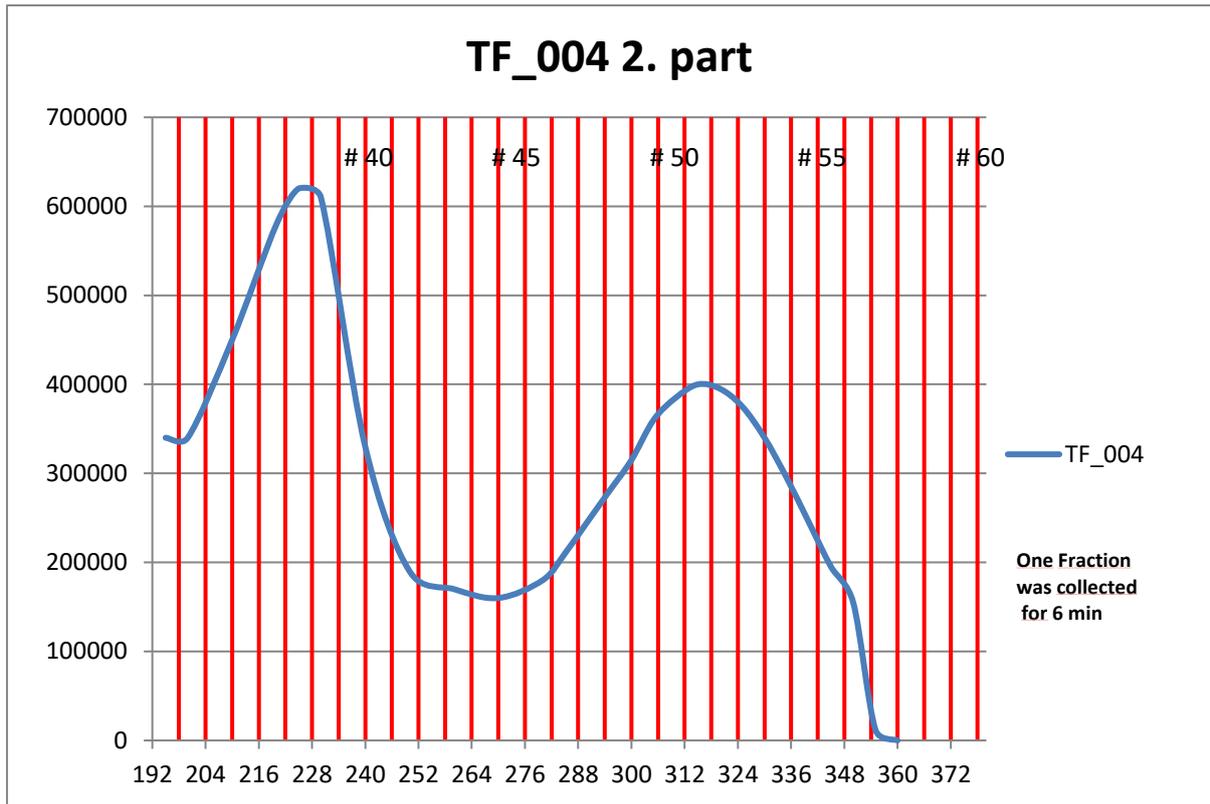
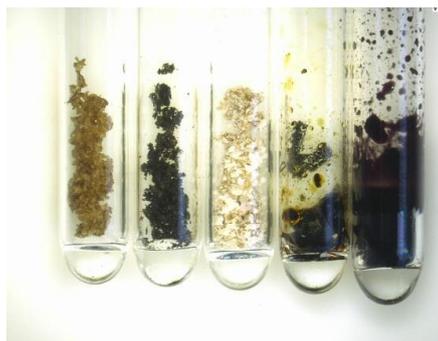


Fig 25: Chromatogram from GPC fractionation of extract using Sephadex G 10

### AP2.1.12. Screening of GPC Fractions

The fraction appears a brown in colour and gave dark colouration when heated to about 70°C. Mixture with the colouring agent (ODB-2) shows a mixed white-brown mixed colour. On heating the mixture to about 100°C, a black colour which compares favourable to the reference was observed (figure 26). This suggests that the fraction contains substances that react with the leuco dye with or without heat.



**Figure 26.**

**Left to Right:**

(1) F4 (UH), (2) F4 (H), (3) F4:ODB-2 (UH),

(4) F4:ODB-2 (H), (5) BPA:ODB-2 (H).

### AP2.1.13. Ultrafiltration of Kraft black liquor

Cross-flow ultrafiltration was performed using a lab scale membrane equipment as reported by. Membrane unit consisted of a Pellicon 2 mini stainless steel cassette holder (Millipore) equipped with a hydrophilic 1 KDa regenerated cellulose membrane (Millipore, USA) with area of 0.1m<sup>2</sup>. The cassette holder comprised two steel plates, one acting as a flow distribution manifold and the other as a mating solid flat surface. A peristaltic pump (LP-1A, Amicon) was used to supply the black liquor from the 2L glass beaker feed tank into the membrane unit. Inlet pressure (feed side) and outlet pressure (retentate side) were controlled by 2 pressure gauges putting into consideration the maximum pressure resistance of the connecting tubes. The operating pressure called transmembrane pressure (TMP) representing the average pressure (bar) difference between the permeate side and retentate side of the membrane was manually controlled by adjusting the retentate valve and calculated using the equation (1)

$$TMP (bar) = \frac{P_{in}-P_{out}}{2} + P_p \quad (1)$$

where  $P_{in}$  and  $P_{out}$  is the inlet and outlet pressure of the membrane,  $P_p$  is the pressure at the permeate side (zero with this system). Prior to sample ultrafiltration, membrane was flushed with deionised water for about 90 minutes to remove the cleaning and storage solution in the system. The original pure water flux was thereafter measured at a flow rate of 0.5 l/min, feed inlet pressure 0.7bar, retentate outlet pressure 0.35 bar. Water was recirculated for about 20mins to achieve stability and constant flow before collection of permeate began. The variation of pure water flux with TMP was also monitored in order to assess the membrane permeability and fouling condition. The retentate solution from the membrane was recycled back into the feed tank and permeate was collected in a glass graduated cylinder. Time taken to collect permeate was monitored with a laboratory stopwatch.

Permeate flux was calculated using equation (2)

$$J = \left(\frac{V}{AT}\right) \quad (2)$$

Where;

$J$  = permeate flux ( $Lm^{-2}h^{-1}$ ),

$A$  = membrane area ( $m^2$ ),

$V$  = permeate volume (L)

$T$  = Time (hrs).

Ultrafiltration was performed at ambient temperature (24°C) with black liquor samples at pH 10 and 5. pH adjustment was achieved by the slow and controlled addition of 5M sulphuric acid to the black liquor. At first, the system was set in recirculation mode to study the influence of TMP on the permeate flux. This also allows for the selection of optimum pressure for the concentration of black liquor. In this mode, both retentate and permeate were recirculated to the feed tank. Permeate was collected every 20 mins after a constant flow was observed. Experiment was then continued in the concentration mode where permeate was continuously withdrawn and recorded until a maximum volume reduction (VR) was achieved. The maximum VR was signalled by the drastic reduction in flux which remained constant over a period. VR was calculated as the ratio between the permeate volume ( $V_p$ ) and the initial feed volume ( $V_o$ ) and expressed in % (eq.3).

$$VR = \frac{V_p}{V_o} \times 100 \quad (3)$$

The experiment was rounded up with diafiltration. This was done to ensure maximum recovery of the targeted components and to obtain a more purified fraction. To achieve this, water of approximately the same volume as permeate removed was added to the retentate and the filtration was continued until completion. After the filtration process, membrane cleaning was done as recommended by the supplier. First, the membrane was flushed with deionized water (30°C) for about 1 hour and then cleaned by recycling 0.1M NaOH solution through the system. Washing was then repeated with warm deionised water. Retentate and permeate were collected until the outflows were no longer coloured. After cleaning, the membrane was stored in 0.1% sodium bisulphite solution in the refrigerator (4°C).

### *Analysis of feed, retentate and permeate*

The feed, retentate, permeate and original black liquor were analysed for total dissolved solids (TDS), lignin content, organic content, density and inorganic elements. TDS was determined by gravimetric method and the density was determined by the pycnometric technique. The organic content was determined by heating the residue obtained from the TDS measurement at 700°C for 5 hours. The amount of organic content was calculated as the difference between the weight of the residue before and after heating at 700°C.

Lignin concentration was measured with a Perkin Elmer Lambda 650 UV/VIS spectrometer using the UV method as described by. Samples were diluted with deionised water and 0.1M NaOH prior to the measurement. Lignin concentration was calculated using the Beer-Lambert relationship (Eq. 4)

$$LC \left( \frac{g}{l} \right) = \frac{A}{b \times a} \times df \quad (4)$$

Where:

LC = Lignin concentration (g/l)

A = Absorbance

a = absorption constant (24.6 g/Lcm)

B = cuvette path length, 1cm

df = dilution factor

The concentration of inorganic elements was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES) with a Thermo iCAP6300 Duo. Prior to analysis, the samples were pre-treated to remove the organic component. 400ul of the sample was pipetted into the reaction vessel and mixed with 6ml concentrated nitric acid and 1 ml

hydrogen peroxide. The mixture was heated for about 30mins under a high-pressure rotor. The final solution after treatment is then diluted to 10 ml and analysed.

## Results of ultrafiltration

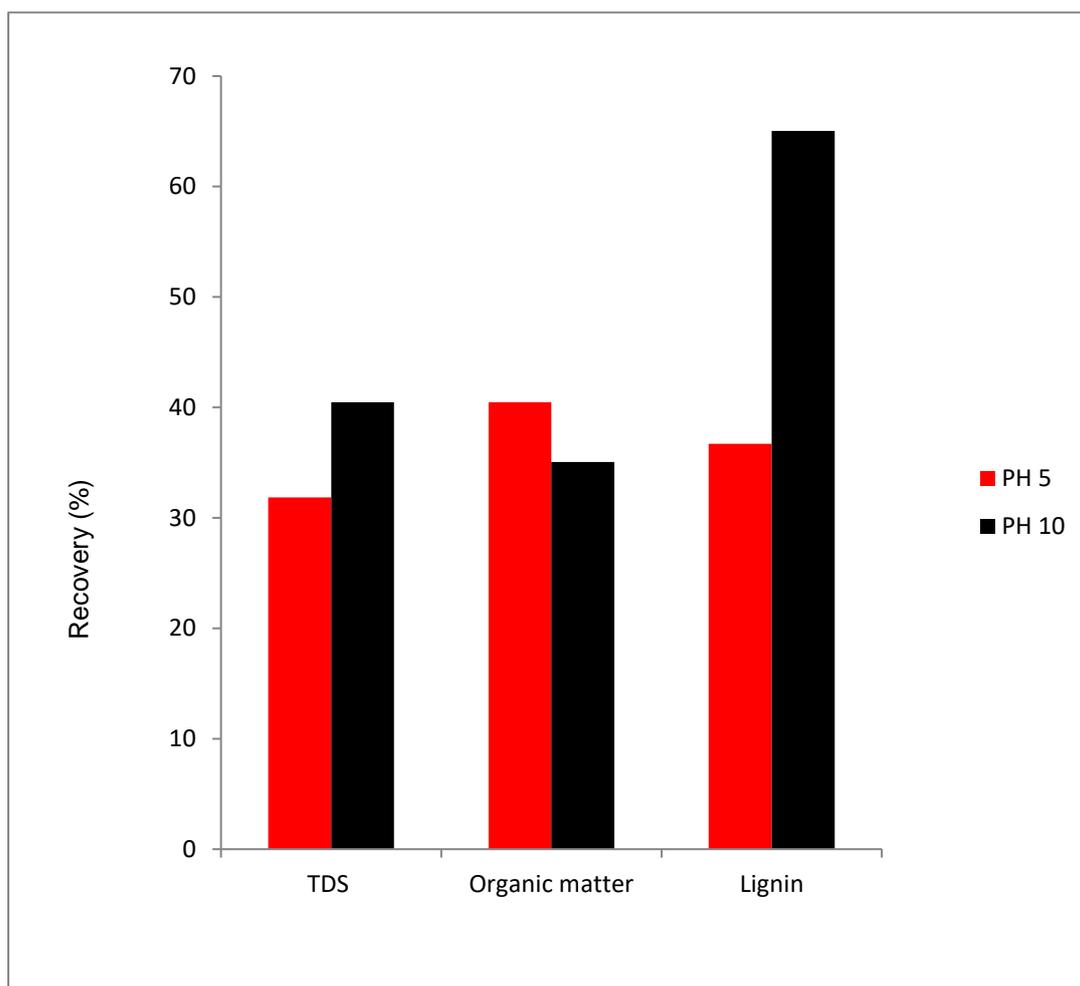


**Fig. 27.** (L-R): original black liquor, retentate and permeate at pH

**Table 9:**

Characteristics of kraft black liquor, feed, permeate and retentate at a VR of 72.5% during ultrafiltration of kraft black liquor with 1KDa regenerated cellulose membrane

	Original black liquor	Feed	Permeate	Retentate	Feed	Permeate	Retentate
pH	13.5		5			10	
Lignin, g/l	103.04	70.15	46.05	93.64	70	45.57	132.76
TDS, %	48.97	43.94	43.07	50.75	26.20	20.07	38.032
Organic matter, %	67.01	31.56	27.29	41.04	52.41	42	66.83
Density, g/l	1279.8	1056.66	1059.95	1063.05	1021.81	1024.55	1035.98
Al, mg/l	23.05	7.18	5.425	16.41	29.35	23.81	29.48
Ca, mg/l	41.21	37.22	21.14	13.45	22.93	15.39	39.63
Cu, mg/l	0.89	0.08	0.6125	1.63	7.55	1.25	3.86
Fe, mg/l	22.14	4.11	3.46	19.86	32.24	24.89	23.54
Mg, mg/l	93.07	86.51	80.2	101.73	40.61	17.82	91.56
Mn, mg/l	29.22	21.85	18.51	26.97	10.11	0.54	31.65
P, mg/l	48.63	51.175	46.87	60.95	30.65	28.51	37.8
Zn, Mg/l	3.82	1.89	1.83	3.59	2.69	1.88	5.34
Na, g/l	33.6	43.06	39.98	47.56	21.9	20.85	23.89
K, g/l	27.121	27.51	25.98	29.63	13.82	13.28	15.29
S, g/l	17.55	42.62	41.01	48.44	14.74	14.06	16.64



**Figure 28.** Recovery (%) of total dissolved solid, organic matter and lignin in the retentate during concentration of kraft black liquor at pH 5 and 10 with regenerated cellulose membrane

#### AP2.1.14. Lignin Fractionation

Hardwood kraft lignin isolated from a kraft black liquor was subjected to a sequential fractionation with green solvent mixtures of differing solubility parameters and hydrogen-bonding capacity. The resultant fractions were thereafter characterized to evaluate their physicochemical properties using FTIR, SEC, DSC, TGA, Py-GC/MS, carbohydrate and elemental compositions. Since the physicochemical properties of lignin differ from one another depending on source and extraction methods, and the affinity of lignin for organic solvents also varies, this process offers an opportunity to obtain lignin fractions of different properties and by extension different interaction capacity with colour former. The scheme of the fractionation is as shown in figure 29.

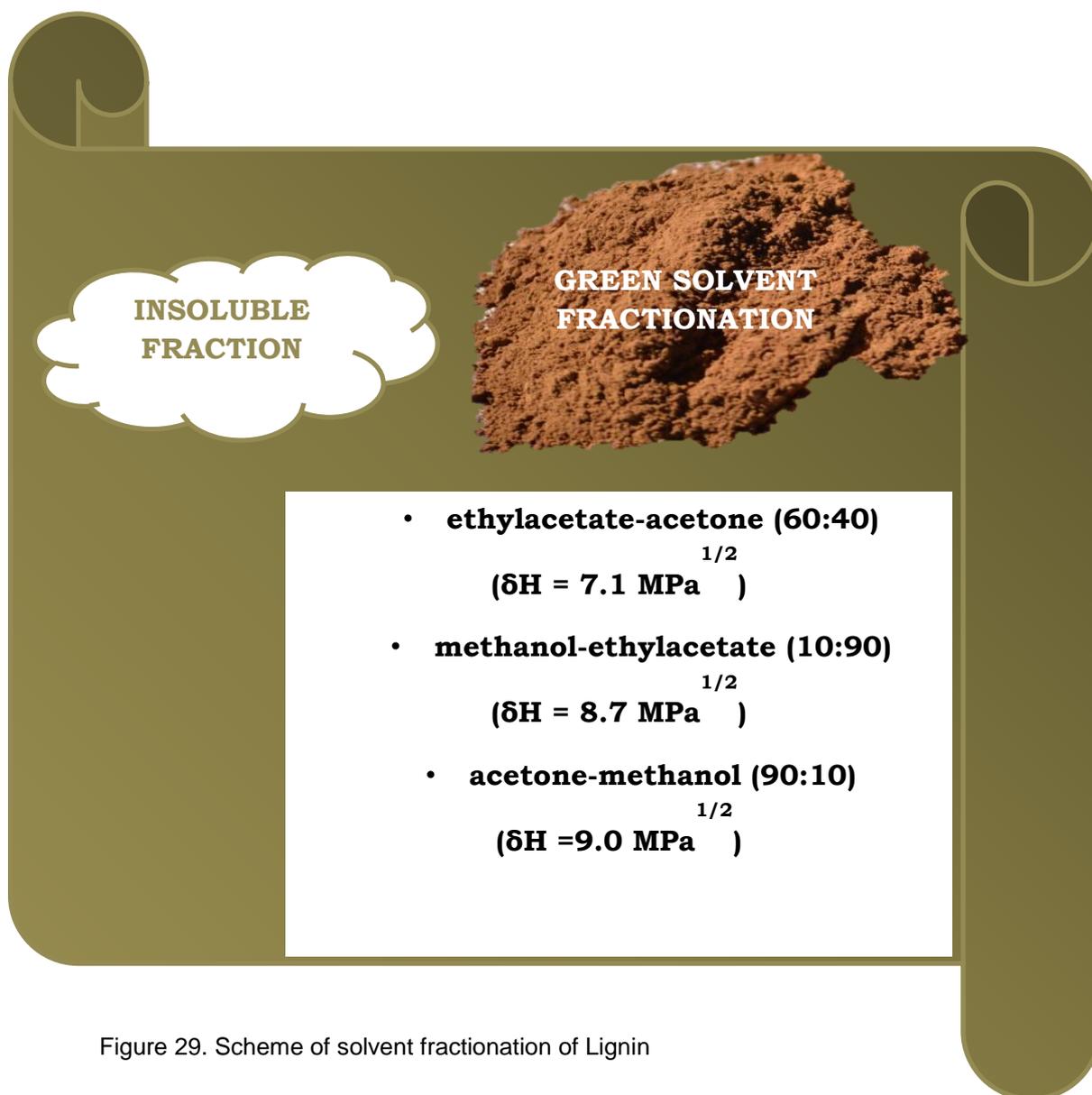
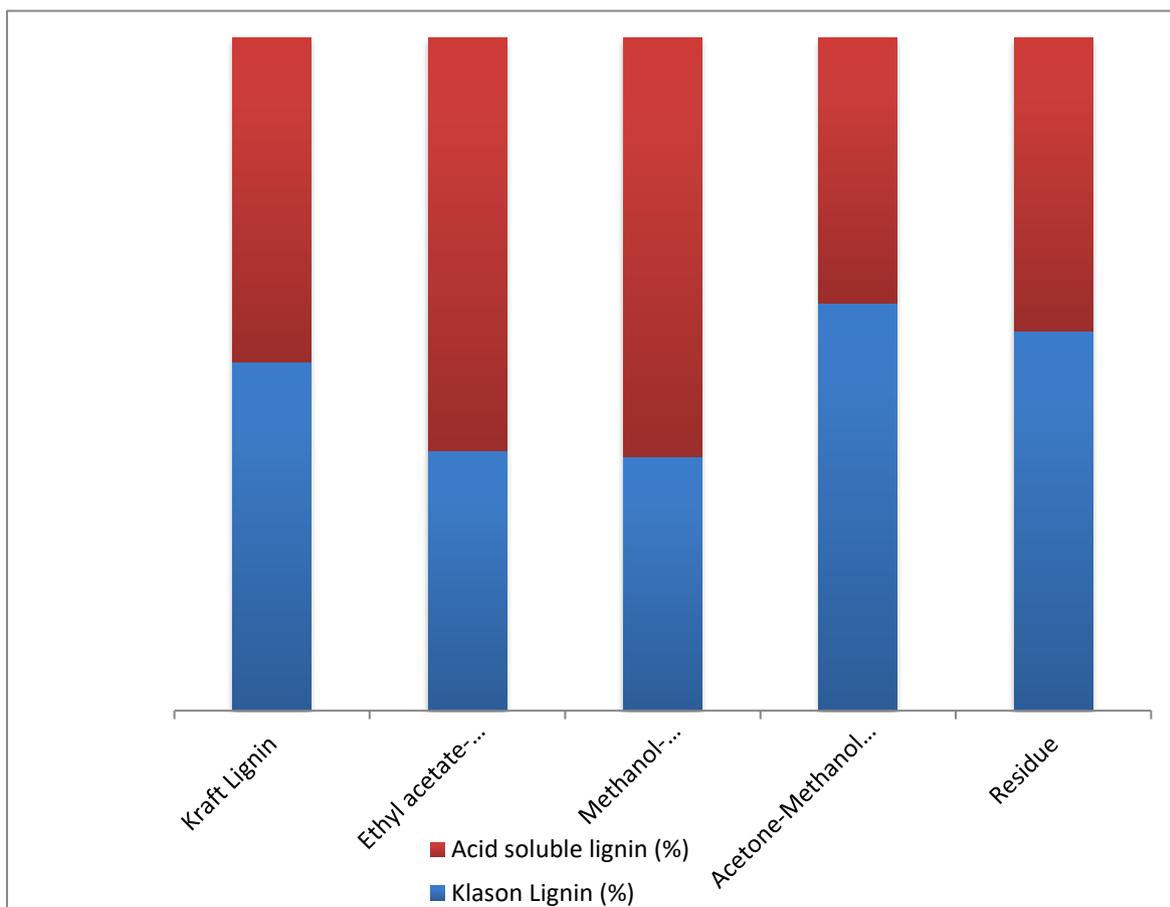
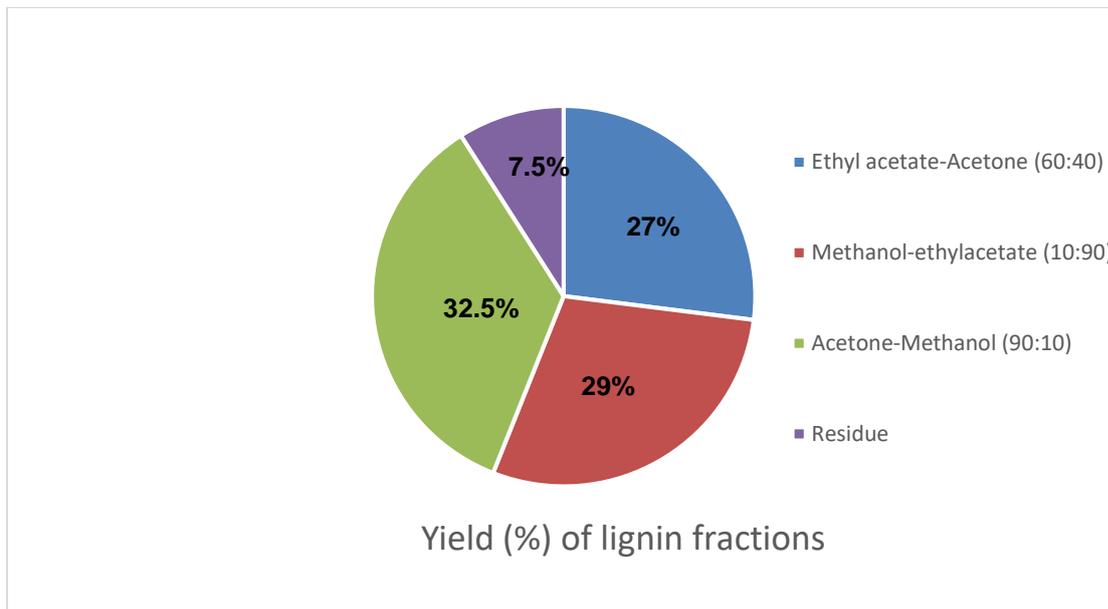
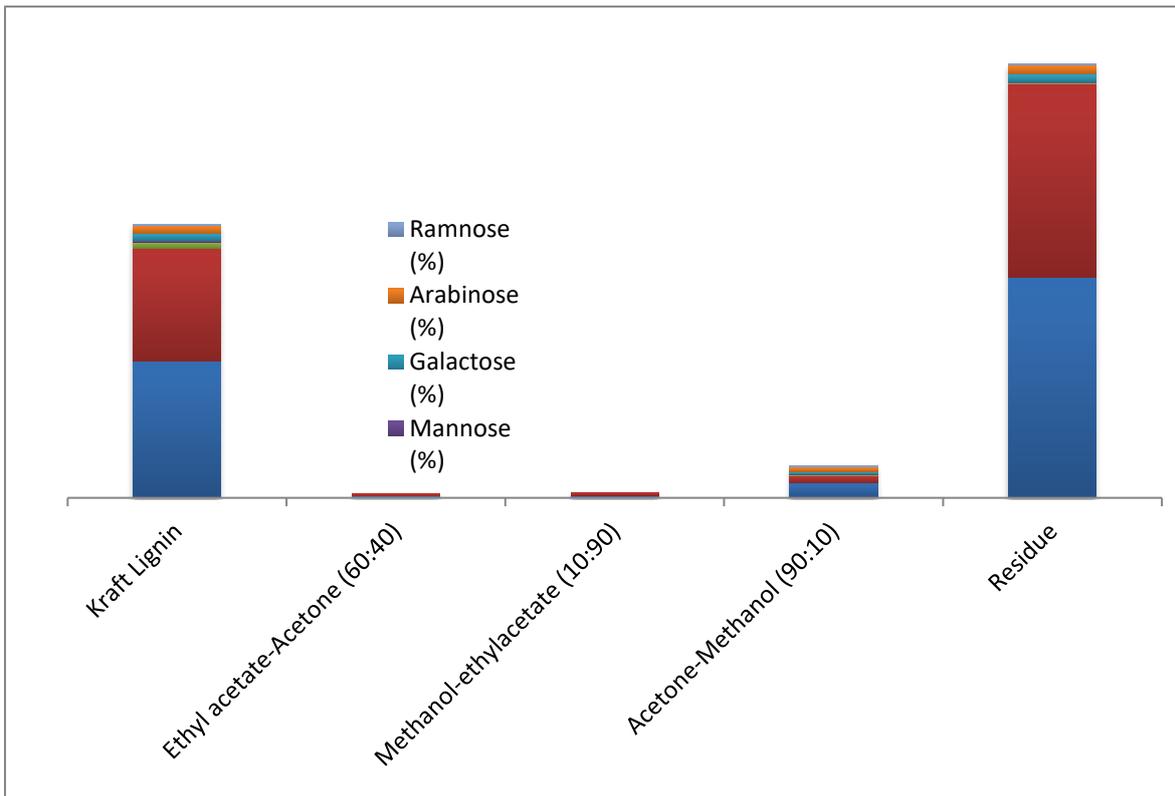


Figure 29. Scheme of solvent fractionation of Lignin

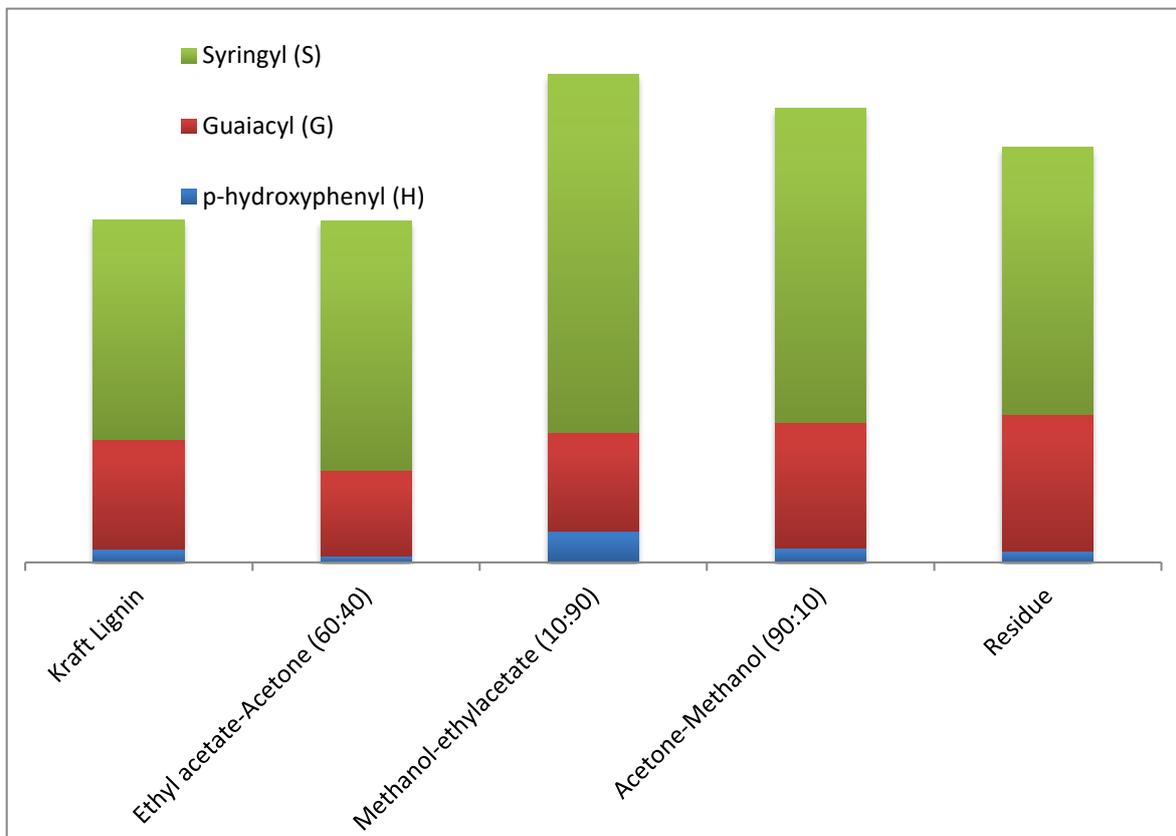
**Results of Solvent fractionation of Lignin**



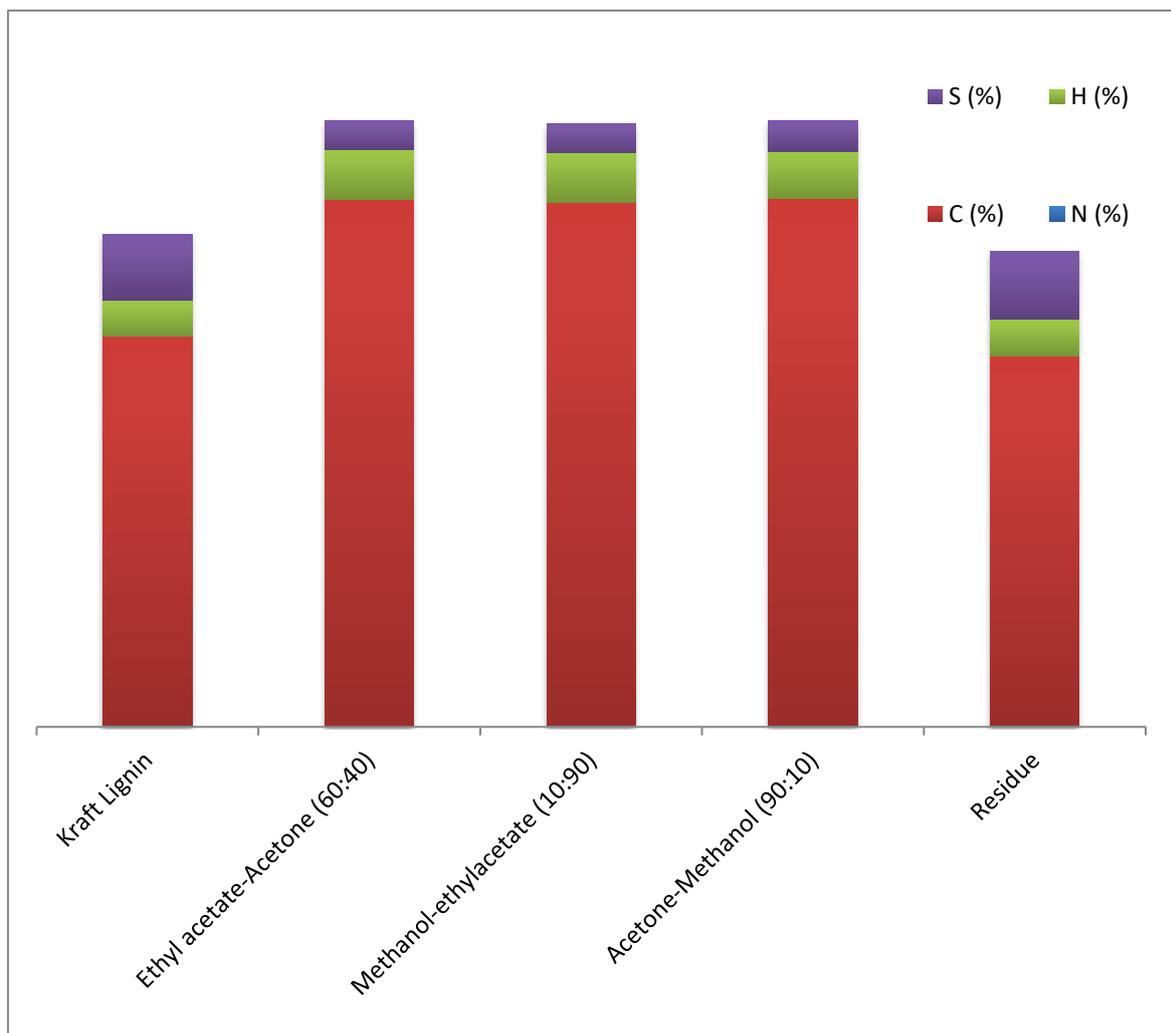
Acid soluble lignin and kraft lignin contents (%) of Lignin fractions



Carbohydrate contents (%) of Lignin fractions



Distribution of lignin degradation compounds in Lignin fractions



Elemental compositions (%) of Lignin fractions

**AP2.1.15. Purification of Tannin:*****Soxhlet Extraction***

To obtain pure tannin fractions, tannin samples were subjected to purification process via Soxhlet extraction. For each extraction, 20 g of raw tannin industrial extract was separated with 150 ml methanol. Extraction was done at the boiling temperature of the solvent and lasted 8 hours. Solvent was thereafter evaporated, and extracts dried in a dessicator for several days. Figure 30 shows the set-up of Soxhlet extraction.



Figure 30. Soxhlet extraction of Tannins

### *Acetone Test of purified tannin*

Purified tannin samples were subjected to acetone test. All the samples produce black colour with ODB-2.



Figure 31. Result of acetone test of purified mimosa extract

## **AP3 Modification**

### **AP3.1 Modification of Carboxymethyl Cellulose (CMC)**

Result of the rapid screening of CMC (API) shows that the cellulosic compound does not function as developer in its pure form and that there is a possibility to improve on its property. To exploit the flexible functionality of CMC, it was subjected to acid hydrolysis. With acid hydrolysis, the Na<sup>+</sup> portion of the Sodium methoxy group is converted to a more reactive -COOH.

Four CMC samples produced by ASHLAND were obtained from our industrial partner, MPE (Table 10).

Table 10: Properties of CMC samples			
Sample code	Degree of Substitution	Viscosity (mPa)	pH
909-1	<b>0.78</b>	<b>6200</b>	<b>8.2</b>
909-2	<b>0.80</b>	<b>1960</b>	<b>7.9</b>
909-3	<b>0.78</b>	<b>3900</b>	<b>7.8</b>
909-4	<b>0.85</b>	<b>3200</b>	<b>7.6</b>

### AP3.1.1. Hydrolysis of CMC

CMC was mixed in water with using the ultraturax (fig 22). Acid hydrolysis was thereafter done with hydrochloric acid solution of varying concentrations (1.5M, 0.1M, 0.01M) for 30mins, 60mins and 120 mins respectively. Glass rod was dipped into each flask to steady the boiling process through controlled stirring. Deionized water was occasionally added to maintain the liquid level. After cooling, the solutions were filled up to the initial volume with deionized water and then centrifuged for 45 minutes at  $5000 \text{ min}^{-1}$ . The supernatant was decanted and the residual hydrolysed Na-CMC was dried overnight in a vacuum oven at  $35^\circ \text{C}$  in the presence of  $\text{P}_4\text{O}_{10}$ . Dissolved Na-CMC was recovered through freeze drying of the supernatant.



Fig 32: Mixing of CMC with Ultraturax



Fig 33: Hydrolysis solution



Fig 34: Freeze-drying of hydrolysed solution



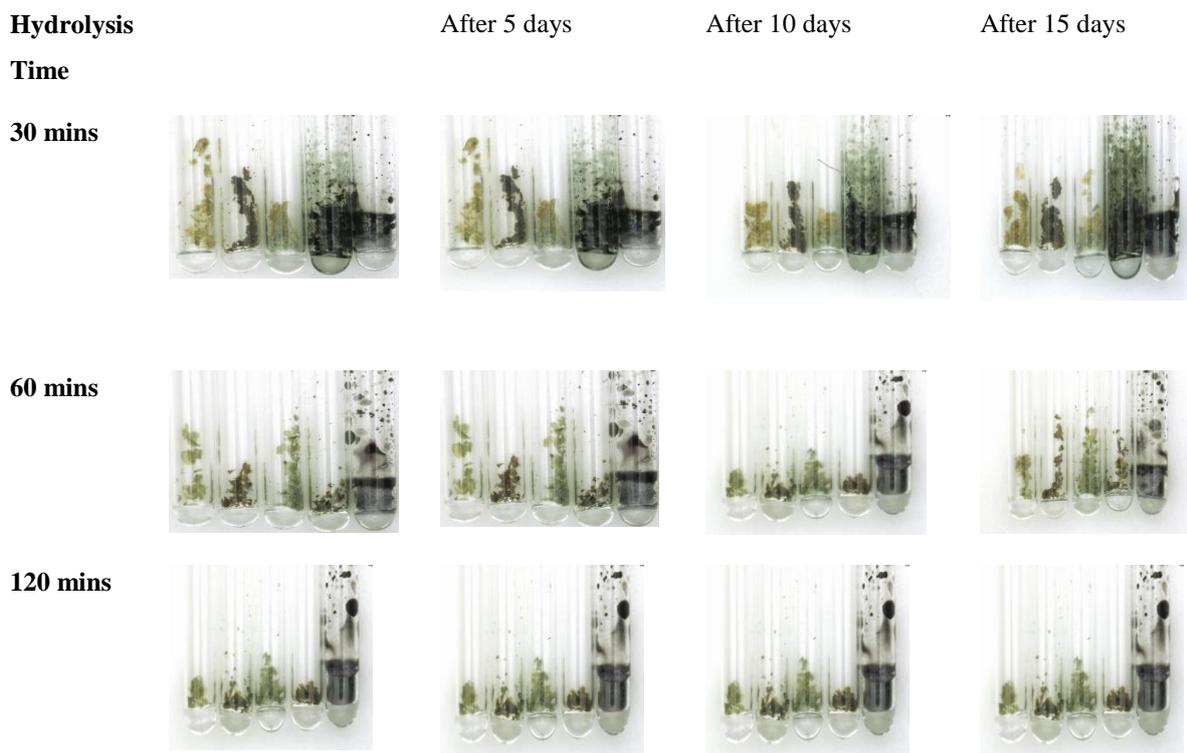
Fig 35: Hydrolysed CMC (H-CMC)

### AP3.1.2. Screening of hydrolysed CMC

Pure Na-CMC and hydrolysed samples were screened using our rapid screening method. Result is presented according to the concentration of acid used (i.e: H-CMC = Hydrolysed CMC from 1.5M HCl). The stability of the colour formed was also monitored for about 15 days.

#### H-CMC<sub>1.5</sub>

Sediments obtained from the hydrolysis of Na-CMC with 1.5M HCl for 30 mins, 60 mins and 120 mins show beige colours. This may be due to the influence of heat and residual acid during vacuum drying. Upon heating to temperature of about 200°C, the samples steadily become dark. Combination of the hydrolysed samples and colouring agent look immiscible without heat. Upon heating, black colour was formed at temperature above 150°C. The colours produced remain stable at higher temperatures above 230- 250°C and also remain stable after 15 days. Sample hydrolysed for 30 mins produced a more intensive colour in combination with the colourant than the other samples.

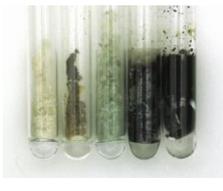
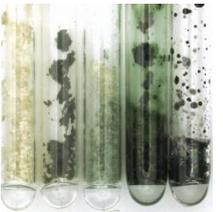
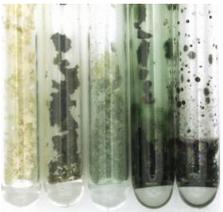
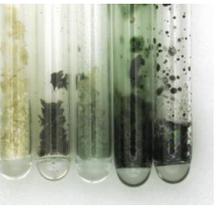


***Left to Right:***

(1) H-CMC<sub>1.5</sub> (UH), (2) H-CMC<sub>1.5</sub> (H), (3) H-CMC<sub>1.5</sub>:ODB-2 (UH), (4) H-CMC<sub>1.5</sub>:ODB-2 (H), (5) BPA:ODB-2 (H).

**H-CMC<sub>0.1</sub>**

The hydrolysed sediment samples were creamy after drying and turned dark on heating at temperature above 100°C. It has to be tested, if the color formation of the hydrolysed CMC is sufficient to be applied in thermal paper without any dye. All three samples formed a green mixture with the colourant without heat and produced a dark colouration on heating but with a splash of green. The cause of the greenish appearance is still unknown. Sample from the 60 mins hydrolysis produced a smoother dark mixture with the colourant.

Hydrolysis Time	After 5 days	After 10 days	After 15 days
30 mins			
60 mins			
120 mins			

***Left to Right:***

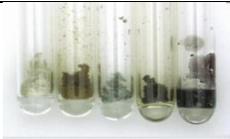
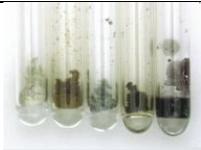
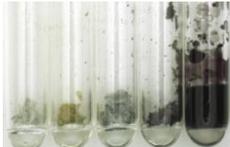
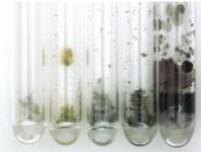
(1) H-CMC<sub>0.1</sub> (UH), (2) H-CMC<sub>0.1</sub> (H), (3) H-CMC<sub>0.1</sub>:ODB-2 (UH),

(4) H-CMC<sub>0.1</sub>:ODB-2 (H), (5) BPA:ODB-2 (H).

## H-CMC<sub>0.01</sub>

### Sediment

Result of screening shows that samples from 30mins and 120 mins hydrolysis time turned deep brown on heating to about 150°C while sample from 60mins hydrolysis time produced a lighter brown colour. All three samples, however, produced usual dark colour reaction in combination with the colourant at temperature above 200°C. The colours were also stable for the first 15 days of study.

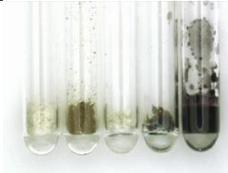
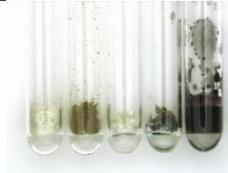
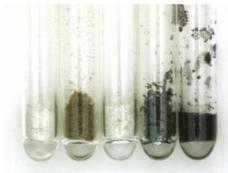
Hydrolysis Time	After 5 days	After 10 days	After 15 days	
30 mins				
60 mins				
120 mins				

***Left to Right:***

(1) H-CMC<sub>0.01</sub> (UH), (2) H-CMC<sub>0.01</sub> (H), (3) H-CMC<sub>0.01</sub>:ODB-2 (UH),  
(4) H-CMC<sub>0.01</sub>:ODB-2 (H), (5) BPA:ODB-2 (H).

## Supernatant

The three supernatant samples show colour response similar to their respective undissolved portions.

Hydrolysis Time	After 5 days	After 10 days	After 15 days
30 mins			
60 mins			
120 mins			

***Left to Right:***

(1) H-CMC<sub>0.01</sub> (**UH**), (2) H-CMC<sub>0.01</sub> (**H**), (3) H-CMC<sub>0.01</sub>:ODB-2 (**UH**),

(4) H-CMC<sub>0.01</sub>:ODB-2 (**H**), (5) BPA:ODB-2 (**H**).

### AP3.1.3. Acid-Methanolysis of CMC

Ca. 1g of pure CMC was introduced into 50 ml of 0.1M HCl under constant stirring. The mixture was heated in a water bath at 60°C for 2 hours. The mixture was cooled and introduced into the round bottom flask. Methanol was added, heated at 80°C for 5 hours and then slowly dried with rotary evaporator to remove the residual acid. Methanol addition was repeated 2 times. The dried hydrolysate was then dried overnight in the vacuum oven at 40°C. Dried sample was milled into fine powder with the Herzogmühle. The time of hydrolysis was varied and hydrolysates were processed in similar way.

909-1a (2hours hydrolysis)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB (130 – 140°C)

909-1b (3hours)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB (160-170°C)

909-2a (2hours hydrolysis)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB (ab 220°C)

909-2b (3hours)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB

909-3a (2hours hydrolysis)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB (160 – 170oC)

909-3b (3hours)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB

909-4a (2hours hydrolysis)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB

909-4b (3hours)



L – R: Unheated pure Na-CMC; Heated pure Na-CMC; Unheated HCMC; heated HCMC; unheated HCMC+ODB; heated HCMC+ODB

### AP3.2 Methylation of Extracts

Three pure extracts (BL, OL, PSL) were weighed into glass vials and dissolved in 10 % tetramethylammonium hydroxide (TMAH). The sample weight ratio of extract to TMAH was 1:49. After weighing, the samples were dissolved in an ultrasonic bath for 5 minutes. The methylated extracts were dried under a stream of nitrogen for 10 minutes and stored overnight in the desiccator via P<sub>4</sub>O<sub>10</sub>. Methylation clearly changes the colour of the extracts as seen below.



*Unmethylated beech and pine extract*

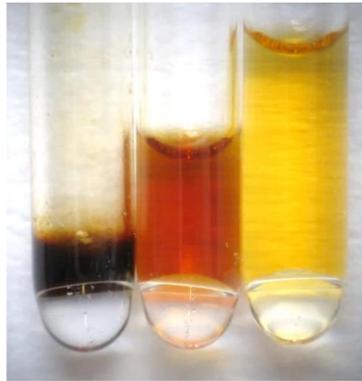


*Methylated beech and pine extracts*

#### AP3.2.1. Screening of Methylated extracts



L-R:  
(1). Methylated beech sulphate extract (**UH**), (2). methylated pine sulphate extract (**H**)



L-R: (1). Methylated organosolv extract (**H**), (2). Beech sulfate extract (**H**), (3). Pine sulfate extract (**H**).



L-R: (1). Methylated Organosolv Extract: OBD2 (**H**); (2) Beech Sulfate Extract: OBD-2 (**H**), (3) Kiefern Sulfate Extract: ODB-2 (**H**)

The methylated organosolv extract turned dark brown at a temperature of 120 °C and above. At a temperature of 200 °C the heating of the methylated organosolv extract was stopped. The two methylated sulphate extracts did not discolour during heating. The orange colour of the beech sulfate extract and the yellow colour of the pine organosol extract were only intensified by the action of heat. The heating of the mixtures of methylated extracts and colorants produced similar results. The two mixtures of Sulfate extracts with colorants did not turn black when heated. This is an indication that the methylation of the sulphate extracts was almost complete. Since the phenolic hydroxyl groups and the carboxyl groups lost their function as proton donors due to methylation, the colorant could not change from the colorless to the colored state. The mixture with the methylated organosol extract, on the other hand, turned dark brown to black. Methylation of the organosolv extract appears to have failed completely. Full characterization of the extracts can provide information about which components are contained in the organosolv extract and which cause the coloration during heating.

### AP3.3 Oxidation of Cellobiose

The result of rapid screening of cellobiose is reported (AP1). To further modify cellobiose, it was subjected to oxidation (Kiely *et al.*, 2008). 6 ml of concentrated (70%) nitric acid (HNO<sub>3</sub>) was placed with a magnetic stir into a 300 ml 3-neck round bottom flask equipped with both a thermometer and a condenser. The contents of the flask were then heated to between 55 and 60°C on a hotplate while stirring. About 2.5 g of sodium Nitrite (NaNO<sub>2</sub>) was added to the flask. Then 5g of cellobiose was added in 2 to 3 portions over a period of 10 minutes. An ice bath was used to minimize the rapid rise in temperature. The temperature was controlled not to go beyond 65°C. The aqueous and strongly acidic oxidation reaction mixture was cooled to room temperature. 25 ml of MTBE was added to the oxidation mixture. The resultant layers were then separated and the aqueous solution was concentrated at 45°C under reduced pressure to give about 5ml of dark brown syrup. Further purification of the syrup proved to be difficult.

Nevertheless, the syrup was mixed with the colouring agent in an aluminium pan and tested with our rapid screening method



Fig 36: Oxidation of Cellobiose



***Left to Right:***

(1) Oxidised sample (UH), (2) Oxidised sample: ODB-2 (H)

Because of the viscous nature of the syrup, the capillary tube could not be used. From the result obtained, a conclusion cannot be yet reached.

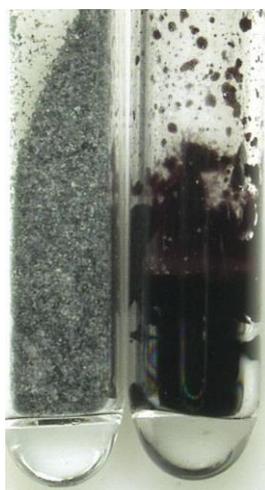
### AP3.4 Bulk polycondensation

Five (5) polymers were synthesised using a vacuum oven according to the following procedure:

1. Pinoresinol (0.11839) was mixed with Mandelic acid (0.0651g) and stearic acid (0.0075g). The three samples were carefully mixed and reacted in a vacuum at 80°C, 50 bar overnight. Resulting product was brown sticky polymer = **POLY1**
2. D-Catechin (0.0098 g) + Succinic acid (0.4458g) + Triethanolamine (0.358 g). 20mg of glycerol was added to the mixture and then reacted in a vacuum oven at 70mbar starting from 80°C and increased to 120°C after an hour. The reaction was allowed to continue overnight. A deep brown viscous liquid was obtained. = **POLY2**
3. D-catechin (0.0043g) was mixed with Citric acid (0.396g). Mixture was treated in vacuum oven as POLY2. A deep brown tacky solid was obtained = **POLY3**
4. Succinic acid (0.0055g) was mixed with Glycerol (0.0030g). The reaction was reacted in same manner as POLY2. A viscous liquid was obtained = **POLY4**
5. Mandelic acid (0.0100g) was mixed with Glycerol (0.0025g). The mixture was treated in same manner as POLY2. A viscous liquid was obtained = **POLY5**

#### AP3.4.1. Screening of Polycondensates

**POLY1** was a brown sticky solid. Milling was quite difficult. Surprisingly, when mixed and heated with the colouring agent, a black powdery product was obtained. The colour obtained, though black, does not signify any melting reaction in relation to the reference. However, a further characterization of the POLY1 will be required to ascertain the nature of the product.



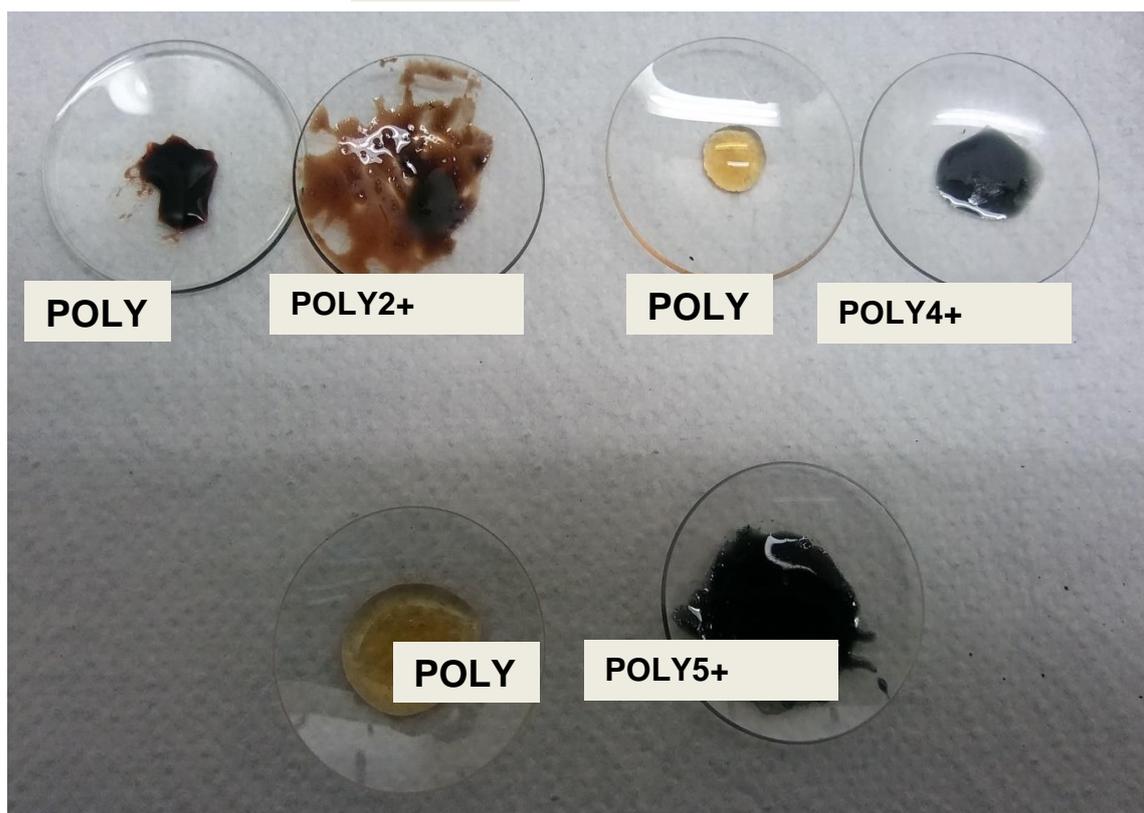
***Left to Right:***

**(1) POLY1:ODB-2 (H), (2) BPA:ODB-2 (H)**

**POLY2** (deep brown), **POLY4** and **POLY 5** (clear) are viscous liquids. They were not amenable with our screening method which requires the use of capillary tubes. The samples were then mixed with the colouring agent on a glass and carefully heated on a hotplate. A dark colouration was observed in the case of **POLY4** and **POLY5** which suggests a reaction between the samples and the leuco dye. **POLY2** however, remained, visibly, unchanged. The temperature of the colour reaction could not be ascertained with this test method.



**POLY2**



### AP3.5 Acetylation of Tannin

Esterification of Tannin was done to introduce ester group to the flavonoid structure of Tannin.

Ca 2g Tannin was dissolved in 20 ml acetone inside a 3-neck round bottom flask. 7ml acetic anhydride and 0.01 ml N-methylimidazole were added. The mixture was then heated under reflux for about 4 hours. After the reaction, the mixture was poured into cold water to precipitate the product. The mixture was centrifuged, supernatant decanted and precipitate was allowed to dry in air for several days. The yield (%) of acetylation was ca 95%. Samples from acetylation were tested by MPE.

### AP3.6 Metal-modified Tannin

Magnesium Tannate was prepared according to the method described by (Zmozinski *et al.*, 2018). 2g of Tannin/Tara was weighed in a Beaker and dissolved in 500 ml of deionized water. After dissolution of the tannin, 20 mL of a 1M Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution was added. The pH was then adjusted to 8 with a 0.5M NaOH solution and the mixture was stirred for about 1 hour. After stirring, the solution was filtered and first dried at 50°C and the drying temperature was raised to 110°C overnight.



Figure 37. Metal-modified Tannins

### ***Screening of modified Tannin***

10 mg of modified tannin sample was mixed with 20mg ODB-2 and 300mg Tetradecanol in a glass tube. Tetradecanol was added to speed up the melting of the mixture. The mixture was heated on heating mantle at 200°C and then cooled in an ice bath. Colour formed was captured with a digital camera.



Figure 37.

From L-R: Tannin only; Tannin+ODB-2; Mg-tannin only; Mg-tannin+ODB-2



Figure 38

From L-R: Tara only; Tara+ODB-2; Mg-tara only; Mg-tara+ODB-2

## Interaction between metal-modified Tannin and ODB-2

The interaction between metal-modified Tannin and ODB-2 was studied with FTIR

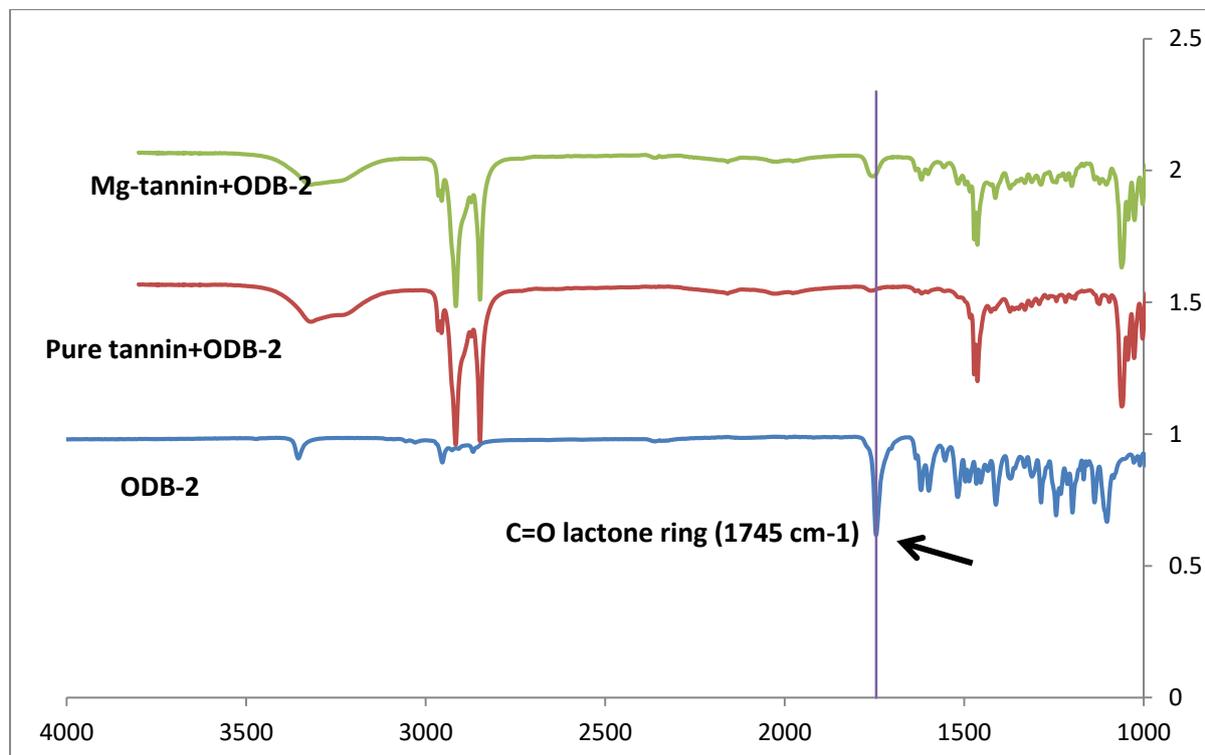


Figure 39. FTIR spectra showing the ring-opening reaction between the metal-modified Tannin and ODB-2

In general, modified Tannin samples show a wide contrast in colour to the pure samples. The yield of modified tannin samples at pH 8 was very high while significantly lower at pH 5. Mg-Tannin Also produced a black colouration on heating with ODB-2. Colour formed is comparable to the colour formed by the pure tannin sample. Mg-Tara did not produce the expected black colour. The black colour seen in the tube is characteristic of the studied tannin samples and not a product of interaction with ODB-2.

Furthermore, FTIR of the pure tannin-ODB-2 confirms the opening of the lactone ring but the C=O band is still visible in the spectra of Mg-tannin. The intensity, though, is severely reduced and the band looks broader. A ring-opening reaction between Mg-tannin and ODB-2 may be assumed. The C=O band was unchanged in the Mg-tara tannin spectra (not shown).

Precipitation of Mg-tannin at pH 5 was largely unsuccessfully as the yield was considerably low. However, test of the tiny fraction obtained shows the formation of black colour when heated with ODB-2 to a temperature of about 200°C.

## Synthesis of Tannin polycondensate

Tannin polycondensates were produced from purified mimosa tannin extract, chestnut extract, grapeseed extract, technical tannin, tara tannin, resorcinol, phloroglucinol and catechol. Samples are as shown in figure 40.



Figure 40. Tannin polycondensates produced from purified mimosa tannin extract, chestnut extract, grapeseed extract, technical tannin, tara tannin, resorcinol, phloroglucinol and catechol

## AP4. Environmental and Health Hazard Check

## AP5. Check Advanced requirements

### AP5.1 Extended Testing

This section gives a detailed output of the extended testing of all samples done by Mitsubishi HiTec Paper Europe (MPE).

Some of the results were left unedited in German as supplied by MPE.

#### AP5.1.1. Modified carboxymethylcellulose

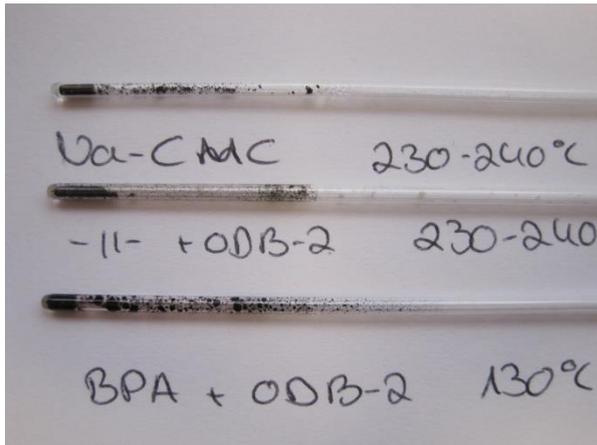
Dispersion of the modified CMC samples (sample TF901-1+ sample 951)), the reference developer (BPA) and a leuco dye were prepared and applied as coat.



CMC sample was heated to 230-240°C, the mixture of NA-CMC and ODB-2 was heated to 230-240°C. Both samples was discolored (black) but the samples doesn't melt. The mixture of BPA and ODB-2 melts at 130°C and turns from white to black.

In the next step a thermal color was produced, the thermal color contains the developer, the leuco dye, pigment, binder and lubricant. These components were mixed and coated on paper. The powder was dissolved in water, the viscosity increased extremely due to the hygroscopicity from this sample. It was not possible to use this dissolved sample in the thermal color.

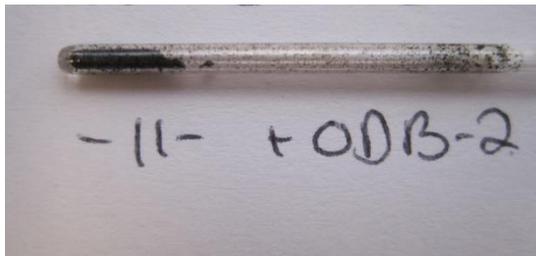
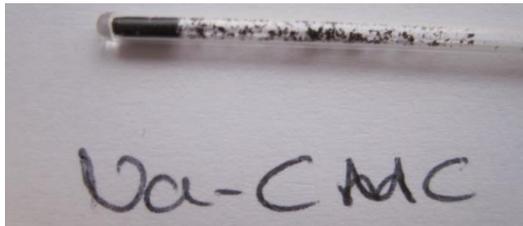
The powder was mixed directly into the thermal color. The thermal color was coated on paper, calendered, after this: print out with a thermal printer: no reaction. Some big particles were detected on the paper

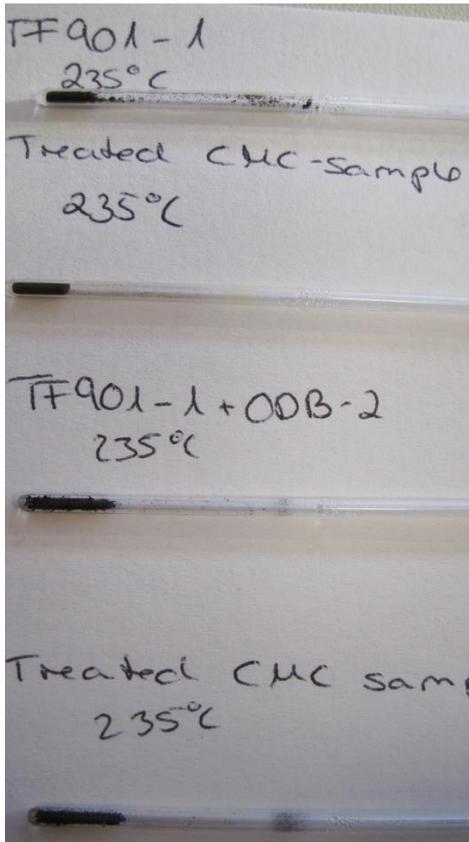


Heated modified Na-CMC (230°C)

Heated modified Na-CMC + ODB-2 (230°C)

Heated BPA + ODB-2 (130°C)



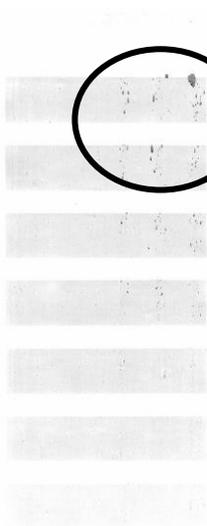


Heated modified Na-CMC TF901-1 (230°C)

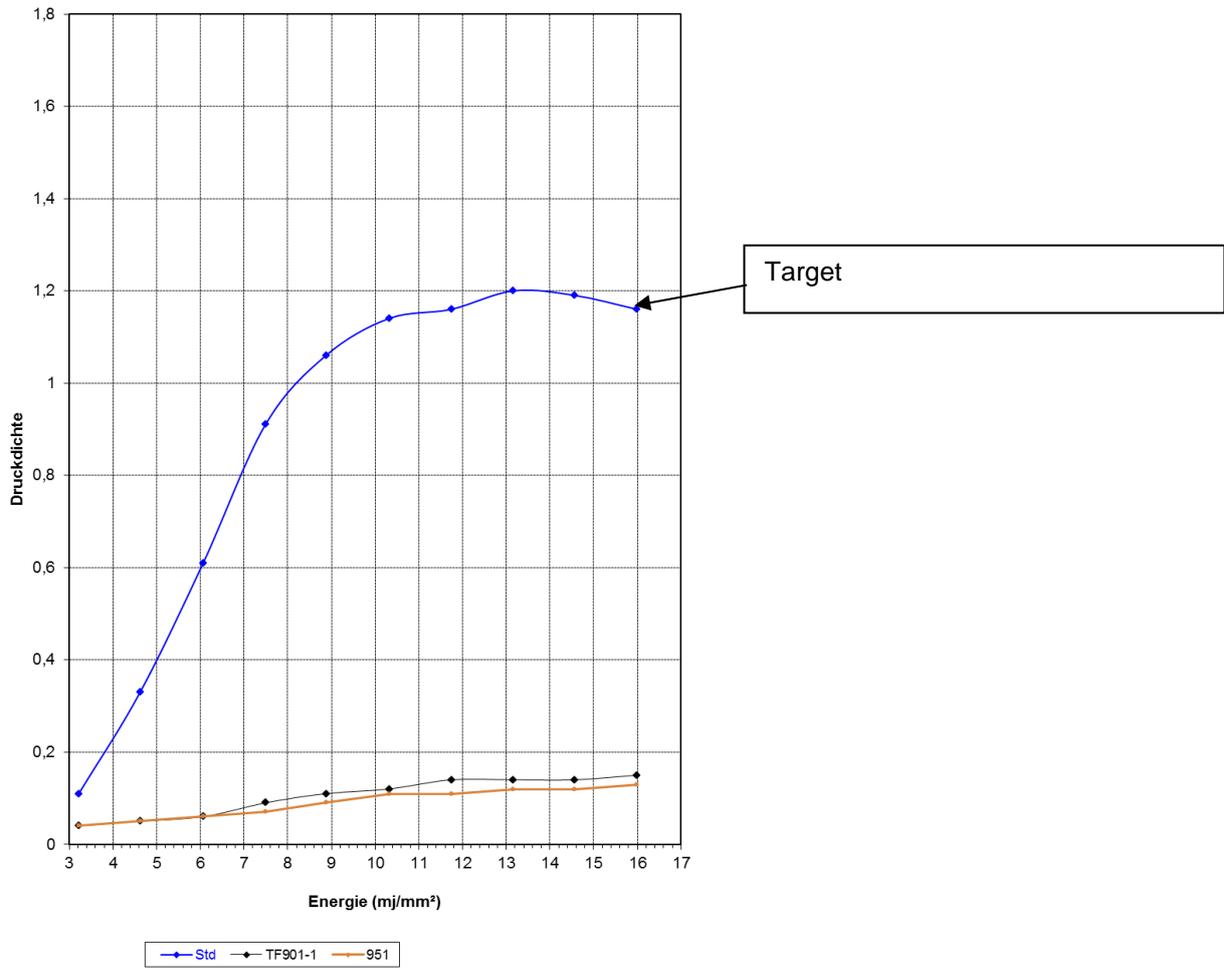
Heated modified Na-CMC 951 (230°C)

Heated modified Na-CMC (TF901-1)+ ODB-2 (230°C)

Heated modified Na-CMC (951)+ ODB-2 (230°C)



Na-CMC used as developer for thermal paper.  
No reaction (highest optical density: 0, 15) target: 1,2  
Big particles in the thermal color.



## AP5.1.2. Tannins

Nr	Name	Schmelzpunkt [°C]	Phenolgehalt [%]
1	Tanal 02	168 bis 170° C	0,99
2	Tanex 20	170 Sublimation	0,86
3	Tanal 40	150-160- sublimation	1,03
4	Tannin	156- sublimation	1,00

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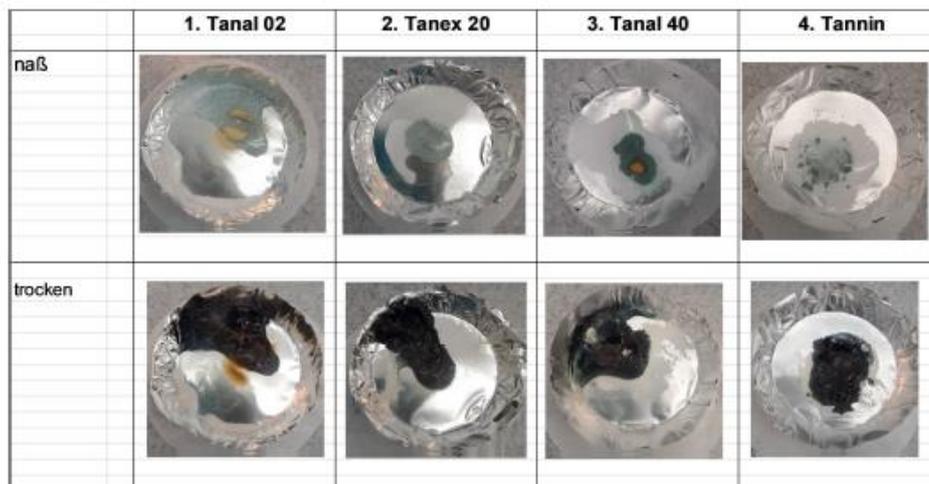


Figure 1: Entwickler Test mit der Farbgeberdispersion

Bei Alle Tannin-Mustern tritt eine Reaktion mit den Farbgeber in der flüssige Phase bereits statt. Dabei ist die Reaktion mit Tanal 40 am stärksten.

Nach der Hitzeeinwirkung reagiert der Farbgeber mit den Tanninen vollständig und die Dispersion nimmt eine satte schwarze Färbung ein. Hierbei sind kaum Unterschiede zwischen den verschiedenen Mustern zu erkennen.

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Figure 2 Entwickler mit Farbgeber Lösung: 2. Tanex 20 3. Tanex 40 4. Tannin



Figure 3: Entwickler mit Farbgeberlösung 1. Tanal 02 beim Abrotieren

Die Aceton Lösungen mit Tannin und Farbgeber sind durchsichtig. Proben 1 bis 3 sind leicht gelb. Das Tannin (Muster 4) zeigt eine leichte lila Färbung.

Nach der Entfernung von Lösungsmitteln im Rotationsverdampfer ist der Rückstand satt schwarz geworden (Figure 4). Dabei reagieren Entwickler mit dem Farbgeber sichtbar und. Es deutet auf einen stabilen Entwickler zu Farbgeber Komplex, da diese Farbe auch nach 3 Tagen bestehen blieb.

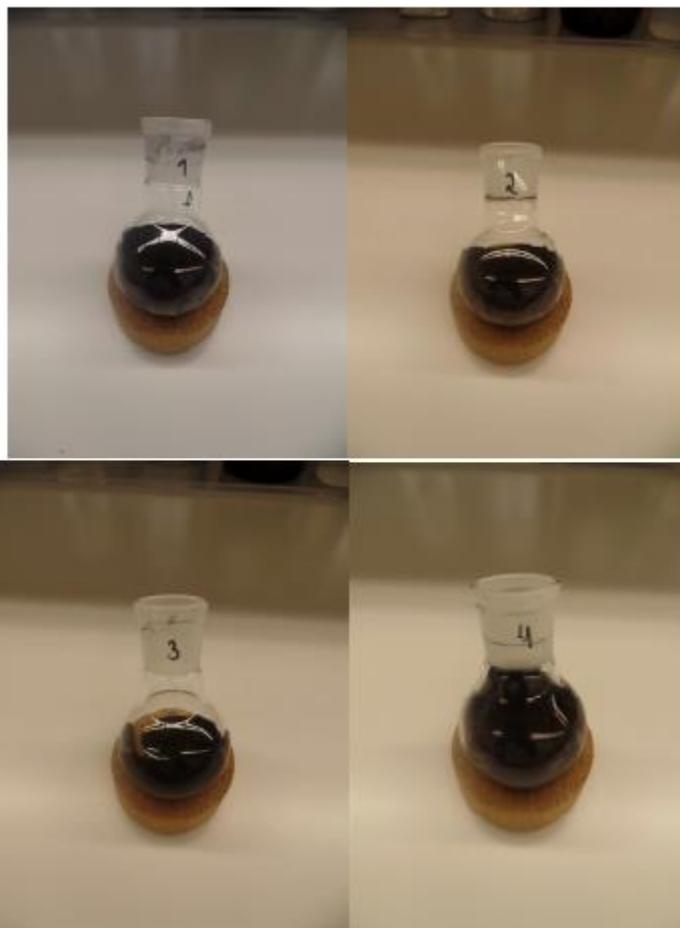


Figure 4 Entwickler und Farbgeber nach der Entfernung des Lösungsmittels: 1. Tanal 02 2. Tanex 20 3. Tanex 40 4. Tannin

- **Thermodruckertest**

*Durchführung:* Die gestrichenen Blätter wurden mit dem Testdrucker Atlantek 400 ausgedruckt. Der Drucker druckt 10 Felder mit ansteigendem Energiestufen von 3 bis 15 mJ/mm<sup>2</sup>. Das Feld mit der maximalen optischen Druckdichte wird angegeben. Die maximal mögliche optische Druckdichte wird mit Hilfe von Hitze eine offene Flamme erzeugt. Dabei wird vorsichtig das Papier kurz über die Flamme gehalten um die Thermoreaktion in Gang zu setzen. Dabei wird besonders beachtet, dass das Papier nicht verbrennt.

Table 3: Eigenschaften der gestrichenen Blätter

Nr.	Muster	Optische Druckdichte Drucker	Optische Druckdichte Hitze	Beschreibung
1	F1+ Tanal 02	0,66	0,96	starkes kleben
2	F1 + Tanex 20	0,07	0,53	kein Ausdruck
3	F1 + Tanal 40	0,55	0,95	starkes kleben
4	F1 + 2 x Tanal 40	0,66	0,97	starkes kleben
5	2 x F1 + Tanal 40	0,69	0,95	starkes kleben
6	Tanal 40+ F1	0,37	0,60	
7	F1+ Tannin	0,64	0,92	Vergrauung
Ref	Thermopapier	1,20	1,20	

Die erzeugte optische Druckdichte der Tannine Proben liegt unter der Referenz. Mit Hilfe von Hitze ist es möglich die optische Druckdichte zu erhöhen, dennoch liegt sie unter 1.

Tanal 02 (Tannic acid) und Tannin zeigen die höchste optische Dichte nach dem Ausdruck mit dem Thermodrucker. Die Verdopplung der Menge an Tannin Tanal 40 zeigt eine Verbesserung der optischen Druckdichte, dennoch nicht ausreichend. Ebenfalls die Verdopplung der Farbgeber zeigt eine leichte Verbesserung der optischen Druckdichte. Eine Veränderung der Reihenfolge beim Auftragen der Komponenten auf dem Papier, zuerst Tannin und dann die Streichfarbe zeigen eine Verschlechterung der Ausdruck.



Acetyliertes Tannin (minimale graue Verfärbung)

Acetylierter Mimosen-Extrakt (keine Reaktion)

Da das Muster TF 824-4-5 (Acetyliertes Tannin) das einzige Muster mit einer minimalen Reaktion ist werden weitere Test nur mit diesem Muster durchgeführt.

Es wurde der Schmelzpunkt vom Muster TF824-4-5 getestet und es wurde getestet ob eine Mischung aus dem Muster und dem Farbgeber Pulver eine Reaktion hervorruft.

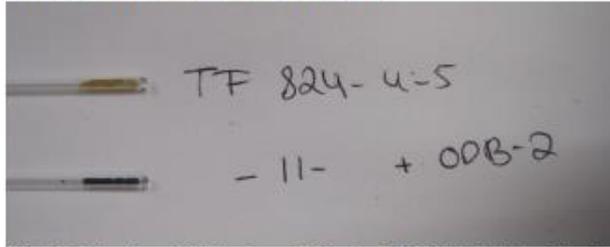


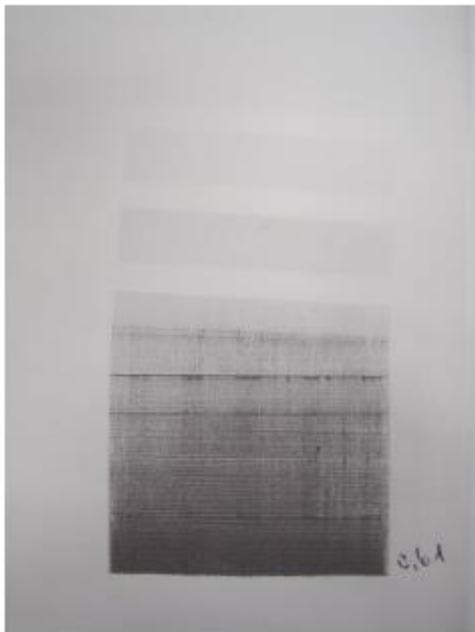
Abb. 3 Schmelzpunktröhrchen mit Muster TF 824-4-5 (Abb. Oben) und mit der Kombination aus TF824-4-5 und dem Farbgeber Pulver (Abb. Unten)

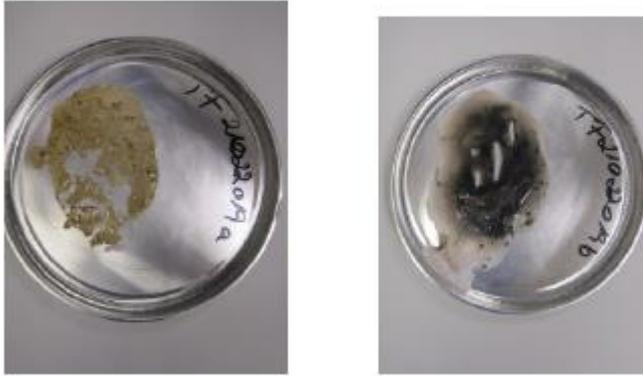
Der Schmelzpunkt liegt bei 141 °C und es findet eine Reaktion zwischen Farbgeber und dem Muster statt. Da eine Reaktion stattfindet wurde eine Streichfarbe hergestellt, diese wurde auf Papier gestrichen und es wurde ein Ausdruck mit einem Thermodrucker erstellt.

#### Herstellen von Streichfarbe und Thermodrucktest

Die fertige Streichfarbe beinhaltet Farbgeber, anorganische Pigmente und Binder. Bei der Zugabe vom TF824-4-5 tritt eine leichte Verfärbung auf. Das Muster wurde unzerkleinert als Pulver zu der flüssigen Streichfarbe dazugegeben.

Nr.	Muster	Optische Druckdichte Drucker	Beschreibung
2	Acetyliertes Tannin - TF824-4-5-5	0,61	Kleben am Druckkopf
Ref	Thermopapier	1,20	





Metallmodifiziertes Tannin (keine Reaktion) Gereinigter Mimosen-Extrakt (grau Schwarze Verfärbung)

Da das Muster TF21022019b Gereinigter Mimosen-Extrakt (Methanolfraktion) das einzige Muster mit einer minimalen Reaktion ist werden weitere Test nur mit diesem Muster durchgeführt.

Es wurde der Schmelzpunkt vom Muster TF21022019b getestet und es wurde getestet ob eine Mischung aus dem Muster und dem Farbgeber Pulver eine Reaktion hervorruft.

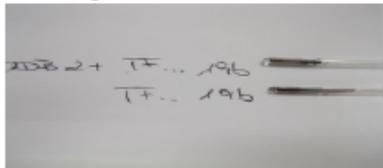


Abb. 3 Schmelzpunktröhrchen mit Muster TF21022019b (Abb. Unten) und mit der Kombination aus TF21022019b und dem Farbgeber Pulver (Abb. Oben)

Bei der Bestimmung des Schmelzpunktes fand keine homogene Schmelze statt. Ab 183°C fing alles an zu schmelzen. Es findet eine Reaktion zwischen Farbgeber und dem Muster statt. Da eine Reaktion stattfindet wurde eine Streichfarbe hergestellt, diese wurde auf Papier gestrichen und es wurde ein Ausdruck mit einem Thermodrucker erstellt.

#### Herstellen von Streichfarbe und Thermodrucktest

Die fertige Streichfarbe beinhaltet Farbgeber, anorganische Pigmente und Binder. Die Substanz TF21022019b ist in Wasser löslich. Nach der Zugabe vom Binder, lies dieser sich nicht unter rühren. TF21022019b verfärbt die Streichfarbe braun. Das Muster wurde unzerkleinert als Pulver in Wasser gelöst und zu der flüssigen Streichfarbe dazugegeben.

Nr.	Muster	Optische Druckdichte Drucker	Beschreibung
2	Gereinigter Mimosen-Extrakt - TF21022019b	0,40	keine Aufälligkeiten
Ref	Thermopapier	1,20	



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- Zusammenfassung

### 1. Metallmodifiziertes Tannin (MagnesiumTannat) - TF21022019a

Das Material ist pulverförmig. Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im nassen Zustand. Dieses Material hat in seiner reinen Form bereits eine dunklere Farbe, diese kann man auf den Bildern wiederfinden. Diese dunklere Farbe ist keine Verfärbung und ist nicht auf eine Reaktion mit dem Farbgeber zurück zu führen.

Es kann keine Thermoreaktion festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im getrockneten Zustand.

### 2. Gereinigter Mimosen-Extrakt (Methanolfraktion) - TF21022019b

Das Material ist pulverförmig. Im nassen Zustand kann eine minimale gräuliche Verfärbung im Kontakt mit der Farbgeberdispersion festgestellt werden.

Nach dem Trocknen kann eine grau schwarze Verfärbung festgestellt werden

In Kombination mit Farbgeber Pulver und unter Hitzeeinwirkung kann eine Reaktion festgestellt werden.

Als Entwickler eingesetzt in einer Streichfarbe kann eine Reaktion festgestellt werden, allerdings ist die Druckdichte nicht ausreichend.

### 3. Acetyliertes Lignin- TF21022019c

Das Material ist pulverförmig. Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im nassen Zustand. Dieses Material hat in seiner reinen Form bereits eine dunklere Farbe, diese kann man auf den Bildern wiederfinden, diese dunklere Farbe ist keine Verfärbung und ist nicht auf eine Reaktion mit dem Farbgeber zurück zu führen.

Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im getrockneten Zustand

### AP5.1.3. Vanillin and vanillin derivatives

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#### Eignung von Vanillin und deren Derivate als Entwickler: 10.12.18

##### Materialien

Nr.	Name	
1. 2291	Vanillin	(4-Hydroxy-3-methoxybenzaldehyd)
2. 2292	Vanillinsäure	(4-Hydroxy-3-methoxybenzoesäure)
3. 2293	Isovanillinsäure	(3-Hydroxy-4-methoxybenzoesäure)
4. 2295	Isovanillin	(3-Hydroxy-4-methoxybenzaldehyd)

##### Eigenschaften

Nr	Name	Schmelzpunkt [°C]	Phenolgehalt [%]
1	Vanillin	82°C	0,69
2	Vanillinsäure	210°C	-
3	Isovanillinsäure	244°C	-
4	Isovanillin	113°C	0,62

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Abbildung 1: Entwickler Test mit der Farbgebersuspension (Naß) 1. Vanillin, 2. Vanillinsäure, 3. Isovanillinsäure, 4. Isovanillin



Abbildung 2: Entwickler Test mit der Farbgebersuspension (Trocken) 1. Vanillin, 2. Vanillinsäure, 3. Isovanillinsäure, 4. Isovanillin

Das Mischen des Vanillins oder deren Derivate mit der Farbgeber in der wässrigen Phase führt zu keiner vorzeitige Farbreaktion Abbildung 1.

Nach dem Trocknen der Suspensionen unter Hitzeeinwirkung reagiert der Farbgeber mit dem Vanillin (1). Dabei entsteht eine schwarze Färbung, charakteristisch für den Farbkomplexbildung. Vanillinsäure (2) und Isovanillin (4) zeigen eine schwache leicht graue Farbe. Bei Isovanillinsäure (3) gibt es sogar keine Farbveränderung.

Möglicherweise zeigt sich hier keine Reaktion zwischen Vanillinsäure (2) und Isovanillinsäure (3) mit dem Farbgeber auf Grund der hohen Schmelztemperatur der beiden Verbindungen.

*Durchführung:* Die gestrichenen Blätter wurden mit dem Testdrucker Atlantek 400 ausgedruckt. Der Drucker druckt 10 Felder mit ansteigendem Energiestufen von 3 bis 15 mJ/mm<sup>2</sup>. Das Feld mit der maximalen optischen Druckdichte wird angegeben.

Mit Vanillin als Entwickler wird eine maximale Druckdichte von 0,6 erreicht. Ziel der Druckdichte ist  $> 1$ . Beim Bedrucken ist einen leichten Vanille Geruch zu erkennen. Vermutlich sublimiert das Vanillin, sowohl beim Bedrucken als auch beim Streichen. Auf dem Papier ist vermutlich weniger Vanillin als eingetragen.

Bei der näheren Betrachtung des Druckbildes ist ein heterogenes Muster zu erkennen. Beim Standard Thermopapier sind die Ausdrücke vollflächig. Mit Vanillin als Entwickler entsteht dagegen ein heterogenes Bild (Abbildung 3)



Abbildung 3: Feld 5 Vanillin

- **Haltbarkeit**

Das gedruckte Papier wurde im klimatisierten Raum 23°C, 50%rF 24h Stunden gelagert und danach erneut die optische Druckdichte gemessen. Nach 24h Lagerung betrug die optische Druckdichte 0,4 (anstatt 0,6). Dies ist ein starker Verlust an optische Druckdichte. Nach 24h Lagerung unter Feuchte Bedingungen (40°C und 90% r.F.) war der Ausdruck verblasst und nicht mehr zu erkennen.

#### AP5.1.4. Citric acid

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Abbildung 1: Entwickler Test mit der Farbgeberdispersion (Oben Naß, Unten Trocken)

Beim Mischen des Farbgebers mit der Zitronensäure ist bereits eine Reaktion zu beobachten.

Diese Verstärkt sich nach dem Trocknen der Suspension.

#### - Thermodruckertest

*Durchführung:* Die gestrichenen Blätter wurden mit dem Testdrucker Atlantek 400 ausgedruckt. Der Drucker druckt 10 Felder mit ansteigendem Energiestufen von 3 bis 15 mJ/mm<sup>2</sup>. Das Feld mit der maximalen optischen Druckdichte wird angegeben.

Mit Zitronensäure als Entwickler wird eine maximale Druckdichte von 0,25 erreicht. Ziel der Druckdichte ist <1.

## AP5.1.5. Ascorbic Acid

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Abbildung 1: Entwickler Test mit der Farbgeberdispersion (Oben Naß, Unten Trocken)

Beim Mischen der Farbgeber Suspension und die Ascorbinsäure ist bereits eine Reaktion zu sehen. Die Streichfarbe wird leicht grau.

Nach dem Trocknet ist die Reaktion intensiver. Der Farbgeber reagiert dunkel.

### - Thermodruckertest

*Durchführung:* Die gestrichenen Blätter wurden mit dem Testdrucker Atlantek 400 ausgedruckt. Der Drucker druckt 10 Felder mit ansteigendem Energiestufen von 3 bis 15  $\text{mJ}/\text{mm}^2$ . Das Feld mit der maximalen optischen Druckdichte wird angegeben.

Beim Bedrucken wurde eine optische Druckdichte von 1,1 erreicht. Der Ausdruck lässt sich gut erkennen (Abbildung 2) .

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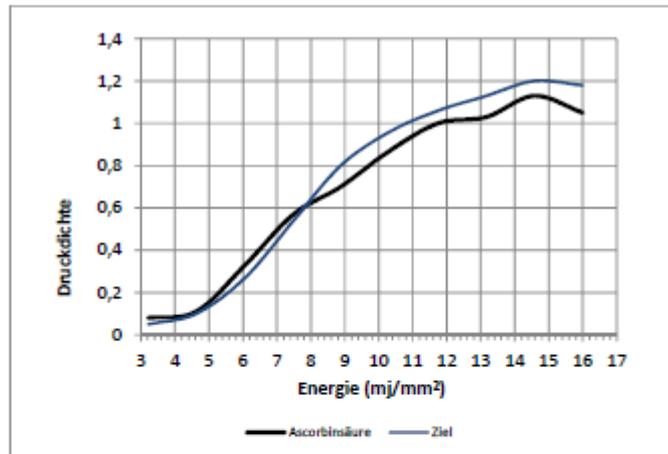


Abbildung 2: Optische Druckdichte in Abhängigkeit vom Energieeintrag

#### - Haltbarkeit

Der Ausdruck wurde auf Haltbarkeitstests geprüft:

Dafür wird ein Ausdruck mit dem Thermodrucker auf höchste Stufe erzeugt. Der Ausdruck wird anschließend auf klimatischen und chemischen Einfluss getestet. Dafür wird der Ausdruck der vor und nach der klimatischen oder chemischen Behandlung gemessen und der Verbleib des Ausdruckes wird gewertet. Dabei wird die Stabilität der Farbkomplex geprüft:

Anfang	Ausdruck Verbleib %
Klimatischer Einfluss auf Haltbarkeit	
Hitze 60°C, 24h	21
Hitze 60°C, 7d	21
Hitze 90°C, 1h	40
Feuchte 40°C, 90%r.F, 24h	24
Feuchte 40°C, 90%r.F. 7d	10 – Kein Ausdruck mehr
Licht 21600 kJ/m²	59

Chemische Einfluss auf Haltbarkeit	Ausdruck Verbleib %
Lanolin 10min	21
Ethanol 25% 20min	33
Weichmacher 24h	27
Wasser 20min	41

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## AP5.1.6. Lignin Fractions



Lignin (Acetonfraktion) (keine Reaktion)

Lignin (Ethylacetatfraktion) (keine Reaktion)

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### - Zusammenfassung

#### 1. Versäuertes Kolophonium - TF824-5-2-2:

Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im nassen Zustand

Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im getrockneten Zustand

#### 2. Acetyliertes Tannin - TF824-4-5-5

Im nassen Zustand kann eine minimale grünliche Verfärbung im Kontakt mit der Farbgeberdispersion festgestellt werden. Nach dem Trocknen kann eine minimale graue Verfärbung festgestellt werden

In Kombination mit Farbgeber Pulver und unter Hitzeeinwirkung kann eine Reaktion festgestellt werden.

Als Entwickler eingesetzt in einer Streichfarbe kann eine Reaktion festgestellt werden, allerdings ist die Druckdichte nicht ausreichend.

Eventuell mehr Potential wenn es mehr Material gibt und das Material in einer Dispersion zerkleinert werden kann.

#### 3. Acetylierter Mimosen-Extrakt - TF554-6-2-2

Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im nassen Zustand, diese Material hat in seiner reinen Form bereits eine dunklere Farbe, diese kann man auf den Bildern wiederfinden, diese dunklere Farbe ist keine Verfärbung und ist nicht auf eine Reaktion mit dem Farbgeber zurück zu führen.

Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im getrockneten Zustand

#### 4. Lignin (Acetonfraktion) - TF908-4-2-2

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Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im nassen Zustand, diese Material hat in seiner reinen Form bereits eine dunklere Farbe, diese kann man auf den Bildern wiederfinden, diese dunklere Farbe ist keine Verfärbung und ist nicht auf eine Reaktion mit dem Farbgeber zurück zu führen.

#### 5. Lignin (Ethylacetatfraktion) - TF908-4-3-3

Es kann keine Farbveränderung festgestellt werden beim Kontakt des Materials mit der Farbgeberdispersion im nassen Zustand, diese Material hat in seiner reinen Form bereits eine dunklere Farbe, diese kann man auf den Bildern wiederfinden, diese dunklere Farbe ist keine Verfärbung und ist nicht auf eine Reaktion mit dem Farbgeber zurück zu führen.

## 2. Verwertung

This project has generated high level of interest particularly from our industrial partner Mitsubishi HiTec Paper Europe owing to the fact that the currently used BPA developer in thermal paper has been placed under restriction by the European Commission. As such, an environmental and health friendly alternative is being sought. Results from the work done so far within the context of this project give room for optimism and positivity regarding the possibility of obtaining BPA alternative from the studied materials.

Particularly, tannin samples are source of bio-based, renewable phenols which can be modified in various forms to function as developer. Nonetheless, Tannin in its pure form gives positive result which we intend to build upon in the next phase of the project. One major challenge facing the use of tannin is the formation of glue with the thermal head while printing as reported by MPE. In addition, tannin is water soluble owing to the large number of polar phenol groups. Modification of tannin is a sure way of reducing the solubility in water. With the formation of a complex with amine or amide, we are hoping that tannin of improved properties in thermal printing will be obtained.

In addition, black liquor is a repository of valuable chemicals that can be modified to produce high value products. Currently, our efforts in this area haven't yielded the expected results. Part of the next phase of the project is to attempt to develop usable compounds from the purified black liquor.

On the economy front, a German patent application has been submitted in conjunction with our industrial partner, MPE. If this goes through, we believe it will bear economic fruits for the University of Hamburg when MPE decides to commercialise some of the usable products. This is still an ongoing area and discussion has been unending.

In general, we are currently working with MPE to decide on the best area of interest for future works. On their own end, MPE are also studying all results obtained so far to see the most promising route for product development.

## 3. Erkenntnisse von Dritten

Results from this project are only known to the University of Hamburg and our industrial partner Mitsubishi HiTec Paper Europe (MPE)

#### 4. Veröffentlichungen

- A German patent application has been submitted. The capture below is the summary of the application.

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### Eisenführ Speiser

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Bremen . 13. Februar 2019  
Unser Zeichen: MA 9455-01DE KUD/UST/ala  
Anmelder/Inhaber: Universität Hamburg  
Mitsubishi HiTec Paper Europe GmbH  
Amtsaktenzeichen: Neuanmeldung

Universität Hamburg  
Mittelweg 177, 20148 Hamburg

Mitsubishi HiTec Paper Europe GmbH  
Niedernholz 23, 33699 Bielefeld

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Wärmeempfindliches Aufzeichnungsmaterial mit Farbwicklern aus nachwachsenden Rohstoffen

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- As part of ongoing global conversation on the need to develop an alternative to BPA in thermal paper, the project team was involved in a workshop on alternatives to Bisphenol A in thermal paper organised by the Belgian public authorities (FPS Economy and FPS Health, food chain safety and environment) together with the European Chemical Agency (ECHA) on 26<sup>th</sup> March 2019.

[Supply chain substitution workshop on alternatives to bisphenol A in thermal paper](#)

- Doctoral thesis planned for next year 2020.