TALL OIL SOLUBILITY IN INDUSTRIAL LIQUORS

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Tall Oil Solubility in Industrial Liquors

Talloljans löslighet i industrilutar

IOANNIS DOGARIS, GUNNAR HENRIKSSON AND MIKAEL LINDSTRÖM

Förord

Denna rapport är slutrapportering av projekt SE213 Studie om löslighet av talloljor i industrilutar inom forskningsprogrammet Resurs- och Klimateffektiv skogsindustri.

Programmets handlar i första hand om energieffektivisering och att kunna nyttiggöra såväl termisk som organiskt bunden energi i pappers- och massabrukens processströmmar. Projekt inom programmet ska ge lösningar på upplevda problem på bruken och ge möjlighet att implementera forskningsresultaten kommersiellt inom en femårsperiod.

Detta projekt har haft som syfte att öka förståelsen av hur kvoten fettsyror/talloljor påverkar lösligheten av talloljorna och att ge praktiska redskap att påverka avskiljningen av talloljor genom tillsats av fettsyror.

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Sammanfattning

Tallolja är en av de mest värdefulla biprodukterna som erhålls vid sulfatkokning av barrved. Den kan användas till ett stort spektrum av tillämpningar inkluderande kemikalier, detergenter och bränsle till förbränningsmotorer och kan därmed till viss del vara ett förnyelsebart alternativ till petroleum. Även om det bara är en bråkdel av vedråvaran som utgörs av tallolja, så blir mängderna avsevärda eftersom sulfatmassa tillverkas i stora volymer. Värdet per ton av tallolja är också förhållandevis högt. Därför är högt talloljeutbyte viktigt av både ekonomiska och miljömässiga orsaker. Syftet med detta projekt är att finna metoder att öka utbytet av tallolja.

Kemisk massatillverkning genom sulfatmetoden kan beskrivas som en cirkulär process, där processkemikalier (NaOH och NaSH, "vitlut") blandas med vedråvaran följt av massakoket varpå den färdiga massan avskiljs från en lösning med utlöst material och delvis förbrukade processkemikalier ("svartlut"), varefter denna i ett trestegsförfarande omvandlas till vitlut. Första steget är en koncentration av svartluten genom indunstning, och det är även under detta steg som värdefulla biprodukter, främst tallolja och terpentin erhålls. Andra steget är förbränning av den koncentrerade svartluten i sodapannan med en smälta av Na_2CO_3 och Na_2S som produkt, som löses upp i vatten, "grönlut". Tredje steget är en omvandling av grönluten till vitlut i kalkcykeln.

Avskiljandet av talloljan sker genom en dekantering ungefär halvvägs in i koncentrationen av svartluten. Utbytet är som sagt mycket viktigt, men ganska lite är känt om vilka parametrar som är viktiga här. En orsak till detta är det komplicerade system som naturliga svartlutar utgör; förutom en komplex blandning av oorganiska salter, innehåller det en stor diversifierad mängd av organiska molekyler, som dels är nedbrytningsprodukter från lignin och polysackarider, och dels naturligt förekommande extraktivämnen i veden, och det är framför allt de sistnämnda som är intressanta i talloljan. Detta medför att det är svårt att ha kontroll på kemiska parametrar i försökmed naturliga svartlutar.

Konceptet i denna studie är att använda ett förenklat system baserat på en "syntetisk svartlut", och en småskalig simulering av talloljeavskiljningen. Detta tillåter att man har hög kontroll på olika parametrar och kan utföra relativt långa försöksserier med måttlig arbetsinsats. Det vi har fokuserat på är kvoten mellan talloljan huvudkomponenter – fettsyror och hartssyror. Resultaten tyder på att de bästa utbytena av tallolja sker när man har högre halter fettsyror i systemet. Data på naturliga kvoter indikerar att halten fettsyror i naturliga talloljor är "för låg", vilket öppnar upp mot möjligheter at öka talloljeutbytet genom att tillsätta mer fettsyror till svartluten före talloljeavskiljningen. Vidare har lignin en komplex betydelse för talloljeavskiljningen, och minskad ligninhalt skulle vara att föredra.

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Summary

Tall oil is one of the most valuable by-products that is produced at kraft pulping of softwood. It has a large spectrum of applications including chemicals, detergents and fuel to combustion engines, and is thus partly a renewable alternative to petroleum. Even if it is just a minor part of the wood that is converted to tall oil, the volumes produced will be large due to the large amounts of kraft pulp that is produced. The value per ton of tall oil is also relatively high. High yield of the tall oil is thus essential both for economic and environmental reasons. The purpose of this study is to develop methods for increasing the yield of tall oil production.

Chemical pulping by the kraft pulping method can be described as a circular process, where process chemicals (NaOH and NaSH, "white liquor") are mixed with the wood raw material and the ready pulp is separated from a solution of dissolved material and partly consumed process chemicals ("black liquor"), where after the black liquor is converted to white liquor in a three-stage procedure. The first stage is a concentration of the black liquor through evaporation, and it is under this stage valuable by-products, such as tall oil and turpentine are produced. The second stage is a combustion of the concentrated ("strong") black liquor in a recovery boiler with a melt of Na_2CO_3 and Na_2S as the product that is dissolved in water forming the "green liquor". The third stage is a conversion of green liquor to white liquor in the lime cycle.

The separation of tall oil is done by decantation approximately halfway through the concentration of the black liquor. The yield is as discussed above very important, but relatively little is known about which parameters are important here. One reason for this is the complexity of the black liquor; in addition to a complicated mixture of inorganic salts, it contains a large diversity of organic molecules that are partly degradation products of lignin and polysaccharides and partly species occurring naturally in the wood. It is mainly the latter, the extractives, that are interesting in the tall oil. This complexity makes control over all chemical components difficult when experimenting with natural black liquors.

The concept in this study is to use a simplified system with a "synthetic black liquor" and a small scale simulation of the decantation of the tall oil, for easier control of different parameters. We have focused on the ratio between the main components of the tall oil – fatty acids and rosin acids. The experimental results indicate that the best results of decantation occur when the proportion of fatty acid is high in the tall oil. Available data on the compositions of black liquors indicate that the contents of fatty acids generally are "too low", and this opens up to the possibility to increase the yield of tall oil by adding fatty acids to the black liquor prior to the decantation.

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I.   Målsättning med projektet

Målsättningen med projektet är att studera hur lösligheten av tallolja i svartlut är beroende av olika parametrar, varav den viktigaste är kvoten mellan hartssyror och fettsyror. En annan fråga har varit ligninets roll. Då metoder att studera detta systematiskt i labskala saknas har stor del av projektet gått till metodutveckling. Givetvis har det varit en förhoppning att resultaten från undersökningen kan leda till förbättringar av utbytet från talloljeseparation.
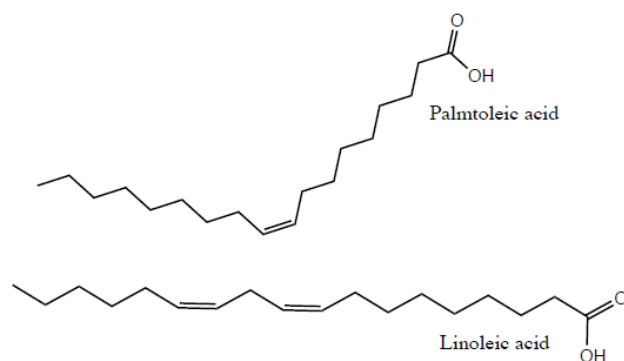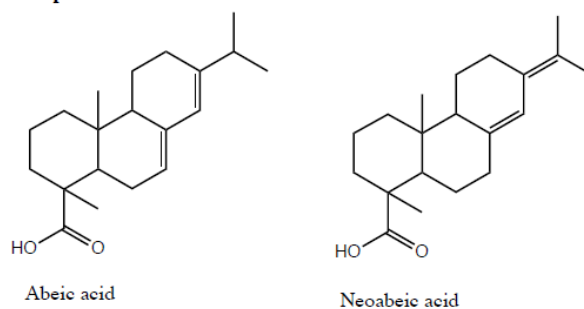
Figur 1. Exempel på amfifila extraktivämnen.

II.   Teknisk och kemisk bakgrund

Vedens kemiska samansättning

Ved består kemiskt sett av fem klasser av ämnen: *cellulosa, hemicellulosa, lignin, extraktivämnen* och *oorganiska ämnen*. *Cellulosan* är för massatillverkaren den mest värdefulla komponenten i veden och är mycket långa kristallina polysackarider bestående av uteslutande glukosrester. *Hemicellulosan* är kortare polysackarider som består av blandningar mellan olika socker och den är också i regel grenad, vilket gör den mer amorf och mindre välordnad än cellulosa. De viktigaste typerna av hemicellulosa är xylan och glukomannan. *Lignin* är en komplex polymer av

aromatiska komponenter som bildar en nätformad struktur med starka interaktioner till både cellulosa och hemicellulosa, inklusive kovalenta bindningar. Tillsammans bildar dessa tre komponenter ett slags kompositmaterial som ger veden dess egenskaper, men det finns också lågmolekylära komponenter i ved – *extraktivämnena* är olika typer av organiska ämnen och de har i regel en komplex samansättning och varierar mellan olika arter. De viktigaste klasserna av extraktivämnen i de träslag som är aktuella för svensk massatillverkning är fettsyror och hartssyror (Figur 1). Notera att dessa ämnen bär på karboxylsyror som vid högra pH är laddade, men samtidigt har en annan del av molekylen som är opolär – molekylerna är med andra ord *amfifila* eller tvålliknande. Denna typ av molekyler har en del som söker sig till vatten, och en annan del som söker sig till "feta" opolära substanser. Förutom dessa amfifila extraktivämnen finns det också mycket hydrofoba (fettälskande) substanser som steroler, men även flyktiga ämnen (terpener m.m.) och vattenlösliga, som lignaner. Amfifila extraktivämnen bildar vid högre koncentration miceler, som kan avskiljas och t.o.m. tvätta ur opolära extraktivämnen ur svartluten. Dessutom finns det oorganiska salter och mineraler i ved, varav kalciumsalter är det vanligaste.

Slow sulphur independent scissoring delignification reaction

Fast sulphur dependent peeling delignification reaction
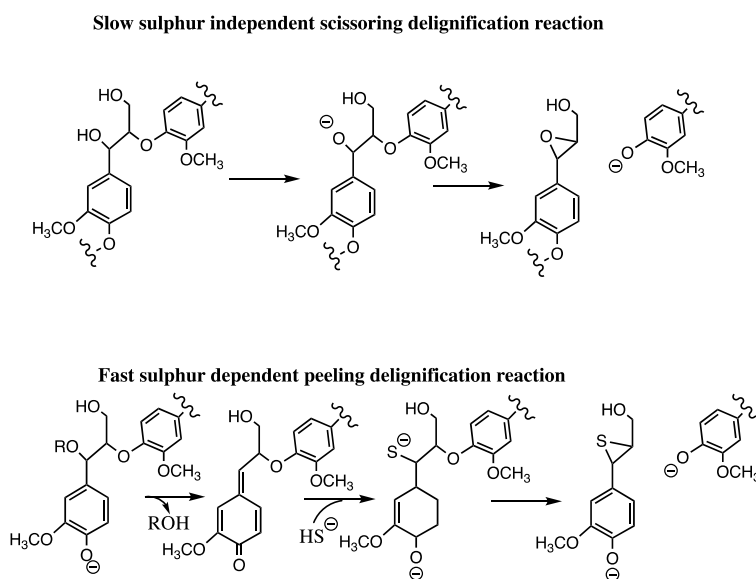
Figur 2. Viktiga ligninnedbrytande reaktioner under sulfatkok.

Sulfatkok

Sulfatprocessen är idag den viktigaste tillverkningsmetoden för kemisk massa, och även pappersmassa över huvud taget. I denna process inkuberas vedflis i vitlut (en lösning av natriumhydroxid och natriumvätesulfid) vid hög temperatur och högt tryck. Under dessa förhållanden bryts det mesta av ligninet ner till lösliga komponenter (Figur 2), som kan reagera vidare i komplexa reaktioner i luten. Detta leder till att fibrerna friläggs och blir mer mjuka och flexibla.
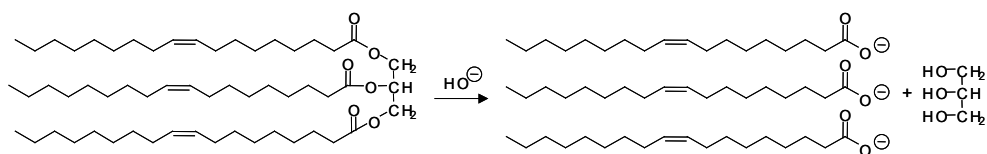
Figur 3. Bildning av fria fettsyror genom hydrolys av estrar.

Olyckligtvis är sulfatkoket inte selektivt för lignin; även polysackarider bryts ner, varpå lösliga modifierade kolhydrater – ofta benämnda sockersyror – bildas. Det är i synnerhet hemicellulosan glukomannan som till stor del förloras under ett sulfatkok. Genom hydrolys av estrar (Figur 3) och nedbrytningen av den komplexa vedstrukturen kommer även extraktivämnen och mineral till stor del att lösas ut i luten, och hamna i svartluten. Massakoket avslutas genom att fibrerna som nu till större delen består av cellulosa med kvarvarande hemicellulosa och lignin avskiljs från svartluten. Massan går vidare till vidare bearbetning medan svartluten går till kemikaliegenereringssystemet.

Svartlutens sammansättning

Svartluten består alltså dels av kvarvarande kokkemikalier och deras produkter (hydroxider, karbonater, vätesulfider, tiosulfater, sulfater etc.), dels av material utlöst från veden, som från början har varit lignin, polysackarider och extraktivämnen. På grund av de mycket reaktiva betingelserna under sulfatkoket, så omvandlas flera av komponenterna ganska kraftigt i lösningen och såväl polymera som lågmolekylära komponenter kan bildas. Detta gäller i synnerhet för lignin och kolhydrater, medan extraktivämnen och oorganiskt material struktur-omvandlas relativt lite. Tabell 1 och 2 ger en överblick av sammansättning i svartlutar.

Tabell 1. Sammansättning av svartlut från sulfatkok av till och björk. (% av torrvikt (Niemelä and Alén 1999).

Komponent	Tall	Björk
Lignin	31	25
Högmolekylärt (>500 Da)	28	22
Lågmolekylärt (<500 Da) f	3	3
Alifatiska karboxylsyror	29	31
Myrsyra	6	4
Ättiksyra	4	8
Andra karboxylsyror (sockersyror m.m.)	19	19
Övriga organiska ämnen	7	11
Exraktivämnen	4	3
Polysackarider	2	7
Övrigt	1	1
Oorganiskt material	33	33
Organiskt natrium	11	11
Övrigt oorganiskt	22	22

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Tabell 2. Karboxylsyrainnehåll av svartlut

Monokarboxylsyror	Tall (barrved)	Björl (lövved)	Eukalyptus (lövved)
Glykolsyra	2.54	2.31	1.99
Mjölksyra	4.20	3.83	2.65
Glycerinsyra	0.13	0.11	0.08
2.hydroxybutansyra2-Hydroxybutanoic	1.04	6.82	2.95
4-hydroxybutansyra4-Hydroxybutanoic	0.19	0.10	0.08
3-deoxytertsyra	0.26	0.59	0.36
2-hydroxypentansyra	0.30	0.15	0.16
3,4- dideoxypentansyra	2.25	1.18	1.21
3-deoxypentansyra	1.46	0.88	0.81
Xyloisosaccharinsyra Xyloisosaccharinic	0.48	3.76	1.90
Anhydrosackarinsyra	0.34	0.18	0.13
3,6- dideoxyhexansyra	0.16	0.56	0.29
3-deoxyhexansyra [c]	0.30	0.30	0.18
Glucosackarinsyra	8.97	4.11	3.48
Dikarboxylsyror			
Oxalsyra	0.13	0.17	0.42
Succinsyra	0.22	0.22	0.33
Metylsucinsyra	0.18	0.04	0.16
Malinsyra	0.16	0.27	0.19
2-Hydroxyglutarsyra	0.39	0.50	0.66
2-Hydroxyadapinsyra	0.43	0.24	0.12
2,5-dihydroxyadapinsyra	0.42	0.22	0.28
Glucoisosackarinsyra	0.47	0.69	0.59

Svartluten har alltså en *mycket* komplex samansättning, som dessutom varierar mellan vedslag, årstid och t.o.m. bruk. Detta gör fenomen relaterade till svartlut svårstuderade, men samtidigt är den förutom att vara utgångsmaterial för energiframställning och vitlutstillverkning även råvara för värdefulla biprodukter. Hittills har det framför allt varit extraktivämnen som tagits tillvara i form av tallolja och terpentin, men även lignin har börjat utvinnas, lignoboostprocessen.

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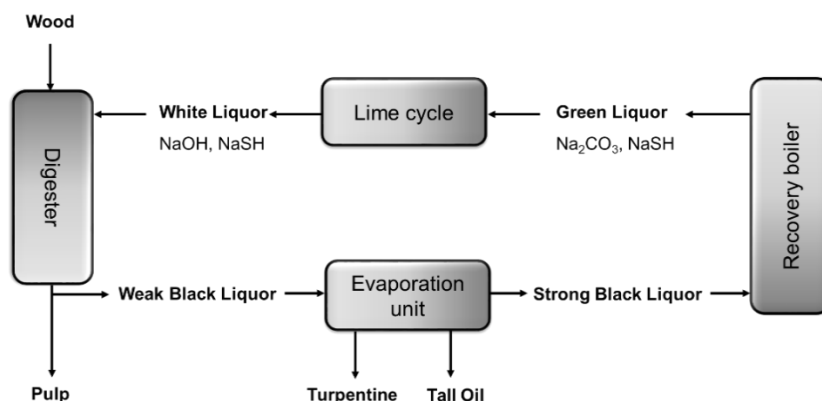
Figur 4. Översikt över kemikalieregenereringen.

Kemikalieregenerering och talloljeseparation

Syftet med kemikalieregenereringssystemet är som diskuterat ovan att återskapa vitlut från svartluten. Detta har givetvis såväl ekonomiska som miljömässiga fördelar och gör det möjligt att använda ett stort överskott av kokkemikalier vid sulfatkoket, vilket är nödvändigt för att bra resultat.

Processen har tre huvudsteg (Figur 4): koncentrering av svartluten (indunstning), förbränning i sodapanna till grönlut (med hög energiproduktion), och omvandling av grönlut till vitlut i kalkcykeln. Det är under indunstningen som värdefulla biprodukter tas till vara. Svartluten koncentreras här genom att exponeras för heta plattor som driver av vatten och andra flyktiga substanser. Värdefull råterpentin och metanol kan tas tillvara från dessa gaser genom destillering. När svartluten uppnått en torrhalt av 25 – 35% har koncentrationen av amifila extraktivämnen och jonstyrka blivit lämpligt för att talloljan ska bilda en särskild fas (micellering) som kan avskiljas genom dekantering.

Talloljan är en av de mest värdefulla biprodukterna som erhålls vid sulfatbruk, men kunskaperna om processteget är till stora delar baserat på empiriska iakttagelser och erfarenheter snarare än systematisk forskning. En svårighet med att studera olika parametrars betydelse har varit svartlutens komplexitet.

III.   Metoder

Vår strategi

Vår grundläggande idé för hur man ska kunna studera olika parametrars betydelse för talloljeseparationen är att istället för att begagna sig av "naturliga" industriella svartlutar, använda en "syntetisk" svartlut, och göra småskaliga försök i provrör. På dessa sätt kan man slippa störande substanser vid detektionen, ha full kontroll över alla parametrar och kunna utföra relativt stora försöksserier. I sin enklaste version består den syntetiska svartluten av oorganiska kemikalier, men andra komponenter kan tillsättas. Samansättningen valdes genom en kompromiss och förenkling av tillgängliga data på svartlutssammansättningar. Nackdelen är naturligtvis att betingelserna till viss del är artificiella och resultat och slutsatser bör så småningom bekräftas av pilotförsök under industriella betingelser.

Tillverkning av syntetisk svartlut

Följande stamlösningar bereds

1. Stamlösning Oorganiska natriumsalter (2.5x koncentration) i avjonat vatten:
   - × NaOH   5.0 g/L
   - × Na_2S 14.0 g/L (or 43.1 g/L of $Na_2S \cdot 9\ H_2O$)
   - × Na_2CO_3 26.4 g/L
   - × Na_2SO_3 5.8 g/L
   - × Na_2SO_4 9.9 g/L
   - × $Na_2S_2O_3$ 11.6 g/L

2. Stamlösning för organiska syror (10x koncentration) i avjonat vatten:
   - × myrsyra   15.0 g/L
   - × ättiksyra   10.0 g/L
   - × mjölksyra   27.5 g/L

3. Stamlösning för xylan (5x koncentration) i avjonat vatten:
   - × Rent xylan (bok)   5.0 g/L

4. Stamlösning fettsyror från tallolja (TOFA, 10x koncentration) i aceton:
   - × TOFA   5.0 g/L

5. Stamlösning hartssyror från tallolja (10x koncentration) i aceton
   - × TOR   5.0 g/L

6 Lignin in form av "lignoboost". Torrt pulver.
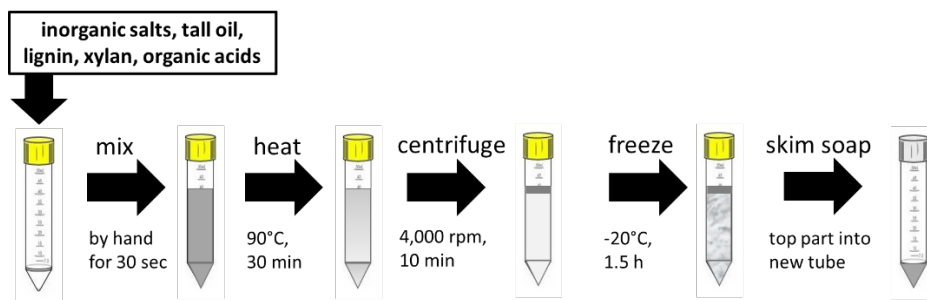
Figur 5. Sammanfattning av de olika stegen i processen

Själva försöken gjordes i satser om 5 ml i 15 ml skruvlocksrör med volymsmarkeringar. Blandningar gjordes enligt följande process:

- Blanda lösningar 4 och 5 efter önskad sammansättning av extraktivämnena i ett 15 ml skruvlocksrör.
- Avdunsta acetonen genom att placera rören i ett varmvattenbad, alternativt torka med varmluft.
- Om lignin ska ingå i experimentet tillsätt 0,40g lignoboostlignin (6) till varje rör.
- Tillsätt 1,2 ml avjonat vatten.
- Tillsätt 2ml lösning 1
- Tillsätt 0,5 ml lösning 2
- Tillsätt 1 ml av lösning 3

- Blanda försiktigt för att undvika skumbildning.

Dekantering

- Inkubera rören vid 90°C i 30 minuter.
- Centrifugera vid 4000 rpm i 10 minuter. En talloljefas kommer nu att bildas överst i röret.
- Märk varje rör vid gränsen för talloljepelleten. Om ingen fas är synlig märk vid 90% av volymen, alltså 4,5 ml.
- Kyl ner och förvara vid 4°C i 24 h.
- Frys rören i 2-3 h vid -20°C.
- Överför den frusna delen ovanför linjen till nya 50 ml rör.

Extrahering av kvarvarande tallolja

- Tillsätt 0,2 ml 1M H_2SO_4 till varje dekanterat prov. pH sänks till 10-11 (från >13).
- Tillsätt 4 ml av 0,2 M pH 9 karbonatbuffert för att justera pH till 9 (undvik att kontrollera pH med pH-meter, p.g.a. förluster).
- Extrahera två gånger med 10 ml metyl *t*-butyl eter (MTBE).
- Poola de två extraktionslösningarna i ett 50-mL rör.
- Indunsta lösningsmedlet genom att placera rören i ett 40°C vattenbad. Undvik högre temperaturer, då kokning etc. kan leda till förluster.

Spektrofotometrisk bestämning av talloljehalt

- Lös upp de intorkade talloljeproven i 2 ml aceton.
- Gör ett blankprov med enbart aceton
- Bered en standard med talloljefettsyror på ca 20 mg (bestäm vikten noggrant).
- Tillsätt 3 ml 5%(W/v) $Cu(II)Ac_2$ till alla rör.
- Tillsätt 5ml hexan till alla rör.
- Blanda kraftigt i 2 minuter.
- Centrifugera 500 rpm i 5 min för att separera faser.
- Mät absorbansen av hexanfasen (den övre) vid 677 nm (och subtrahera absorbansen vid 497 nm (baslinjen).
- Beräkna mängden tallolja med hjälp av kalibrerkurvan (se nedan).
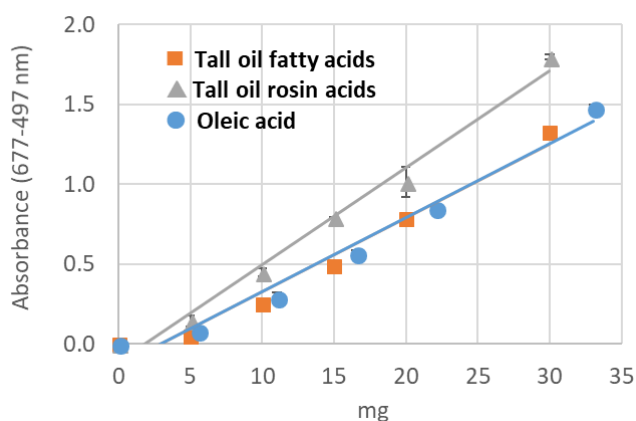
Figur 6. Standardkurvor enligt den spektroskopiska metoden.

Beräkning av talloljehalt

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Lösningar av 0 - 30 mg av talloljefettsyror och hartssyra och oleinsyra bereddes i aceton och analyserades enligt den spektrometriska metoden beskriven av Sitholé (1993) (se ovan). Standardkurvor var av god kvalitet (R^2 i intervallet 0.97 – 0.98) (fig 6). Statistisk behandling av data gav följande resultat for absorbansberoendet hos substanserna:

Talloljefettsyror

Absorbans (677-497 nm) = 0.0460 * mg – 0.1302 **Eq. 1**

Hartssyror

Absorbans (677-497 nm) = 0.0605 * mg – 0.1074 **Eq. 2**

Oleinsyra

Absorbans (677-497 nm) = 0.0461 * mg – 0.1312 **Eq. 3**

Beräkning av talloljeutbyte

Talloljeutbytet % (*SR*) beräknades enligt följande ekvation:

$$SR\ (\%) = \frac{mg\ of\ estimated\ tall\ oil}{mg\ of\ total\ tall\ oil\ in\ black\ liquor}$$ **Eq. 4**

Talloljeutbytet kan beskrivas enligt ekvation 5 där r är kvoten fettsyra till hartssyra.

$$SR(r) = SR_0 + \frac{SR_{max}}{1+e^{-k(r-r_m)}}$$ **Eq. 5**

S är talloljeutbytet i % torrviktsbas. R är kvoten fettsyror till hartssyror (vikt), k är en konstant som bestämmer kurvaturen av modellen, r_m är inflektionspunkten vid vilken utbytesökningen når sitt maximalvärde.

IV.   Resultat och diskussion

En stor del av projekttiden gick åt till att utveckla och bekräfta pålitligheten i ovanstående metod. För en detaljerad diskussion av denna process hänvisas till den engelska rapporttexten. Sammanfattningsvis kan det sägas att metoden visades vara robust och pålitlig för simuleringar av talloljeutbyte inom realistiska kvoter av hartssyror och fettsyror.
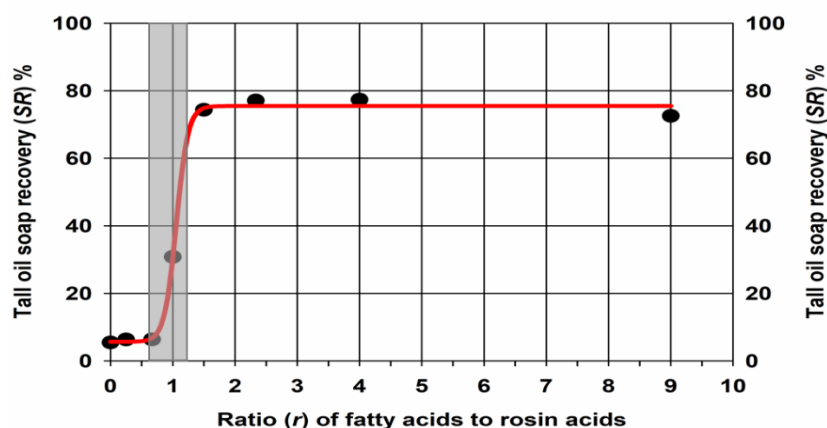
Figur 7. Resultat av experiment med varierande kvot fettsyror-hartsyror.

Effekt av kvoten fettsyror – hartssyror på talloljeutbyte

Försök enligt ovanstående protokoll med varierande kvot hartssyra-fettsyra utfördes och resultatet visas i figur 7. Stora utbytesskillnaderna sker alltså mellan 40 – 60% fettsyror, och därmed kan i princip tillförsel av fettsyror öka utbytet. Detaljer ges i tabell 3.

Tabell 3. Talloljeutbyte i syntetiska svartlutar med blandningar av fettsyror och hartssyror (duplikat).

#	TOR (% av olja)	TOFA (% av olja)	TOFA-TOR kvot	Tall oil recovery (% av olja)	Standard deviation
1	100	0	0.0	5.4	0.1
2	80	20	0.3	6.3	0.6
3	60	40	0.7	6.3	0.0
4	50	50	1.0	30.8	0.1
5	40	60	1.5	74.3	3.8
6	30	70	2.3	77.1	2.1
7	20	80	4.0	77.4	1.9
8	10	90	9.0	72.6	2.7
9	0	100	-	76.3	1.0

Om Ekvation 5 (Eq. 5) används för experimentdata nås en god anpassning (Eq. 6) Data plottas i figur 8

$$SR(r) = 5.64 + \frac{69.86}{1+e^{-10.56\,(r-1.05)}}$$

Eq. 6

(R^2 = 0.998; standardavvikelse 1.974; P < 0.0001)

Eq. 6 förutsäger att maximalt talloljeutbyte vid användning av metodiken i denna studie är s 5.64 + 69.86 = 75.50%, medan ett minimum (när r = 0, alltså inga fettsyror

närvarande) är 5.64%. Vidare visas att invektionspunkten för kurvan är när r = 1.05, vilket innebär att utbytet vid ökad fettsyrehalt så ökar utbytet långsammare för att avstanna vid r i intervallet 1.5 - 2.0. Då r i industriella svartlutar ska typiskt vara i intervallet 0.7 to 1.3 (markerat med grått i figuren) (Uloth et al. 2009; Lenz 1977), så finns alltså goda möjligheter att öka talloljeutbytet genom tillsatts av extra fettsyror. Tabell 4 visar beräkningar för ökat talloljeutbyte.

Tabell 4. beräknat talloljeutbyte (SR) % i svartlutar med olika kvot fettsyror och hartssyror (r) enligt Eq. 6.

r	SR (%)
0.70	7.3
0.80	10.3
0.90	17.5
1.00	31.6
1.10	49.6
1.20	63.6
1.30	70.8
1.40	73.8
1.50	74.9
1.60	75.3
1.70	75.4
1.80	75.5
1.90	75.5
2.00	75.5

Betydelsen av lignin för talloljans löslighet

Ovanstående resultat erhölls alltså med en syntetisk svartlut med kraftigt förenklad samansättning. För att studera ligninets betydelse för talloljeavskiljning, gjordes en serie experiment där olika mängder av svartlutslignin löstes i tallolja med en "realistisk" samansättning av hartssyror och fettsyror.
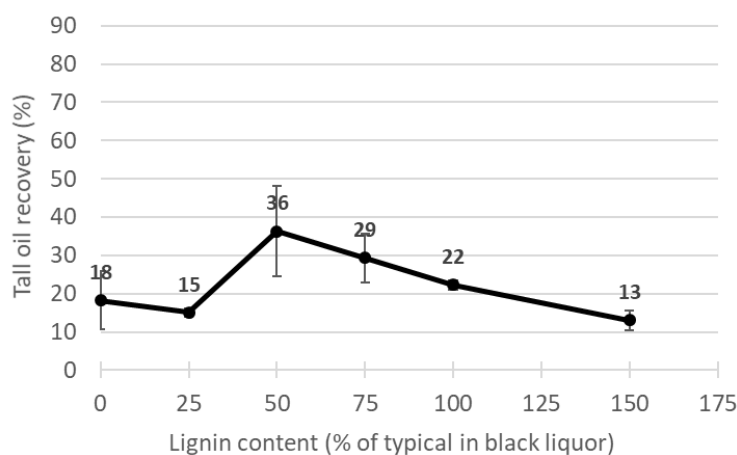
Figur 8. Resultat av experiment med varierande ligninhalt för talloljeutbyte. Vid detta experiment var kvoten hartsyror fettsyror 1. 100% lignin motsvarar förväntad mängd lignin i industrilla svartlutar.

Resultatet (Figur 8) visar att den generella trenden är att ju mer lignin som tillsätts (från 50%) så är talloljans utbyte avtagande. Detta kan möjligen förklaras med att ökad viskositet och hydrofobicitet, som minskar förmågan att bilda avskiljbara miceler av fettsyrorna och hartssyrorna. Å andra sidan, vid låga ligninhalter (0-25%) minskar talloljeutbytet igen. Denna effekt är mer svårförklarad, men lignin skulle möjligen kunna ha en positiv effekt genom att binda till hartssyror – som strukturellt påminner lite om lignin. Detta försök föreslår ändå att man skulle försöka minska halten lignin i svartluten före talloljeseparation.

Slutsatser

1. Ett modellsystem för talloljeseparation har utvecklats som möjliggör studier av olika parametrars betydelse.

2. Tillsats av fettsyror före talloljeseparationen kan vara ett sätt att öka talloljeutbytet.

3. Avlägsnande av lignin före talloljeseparationen kan vara ett sätt att öka talloljeutbyte.

Tekniska lösningar

Det förefaller alltså som om tillsats av "extra" fettsyror kan öka talloljeutbyte, men hur ska detta göras på bästa sätt? En metod skulle vara att tillsätta någon form av billig triglycerid och hydrolysera denna till fettsyror – detta skulle exempelvis vara konsumerad frityrolja från restauranger. En annan intressant möjlighet skulle vara att få talloljor "i retur" från företag som raffinerar tallolja. Denna strategi har fördelen att inga "främmande" fettsyror kommer i cirkulationen.

Det verkar också gynnsamt att minska halten lignin i svartluten före talloljeseparationen. Det finns flera sätt att göra detta såsom lignoboosttekniken och ultrafiltrering av tallolja, och det finns som nämndes i inledningen ett stort intresse för att plocka ut lignin för att använda denna som en resurs medan man samtidigt minskar trycket på sodapannan. Om ligninet kan avlägsnas före talloljeseparationen kan en tredje fördel – ökat talloljeutbyte, möjligen läggas till listan.

Det ska understrykas att dessa experiment är baserade på modellsystem, och bör ses som utgångspunkt för storskaliga försök snarare än definitiva slutsatser.

1 Introduction

1.1 BACKGROUND

For several reasons, it is crucial to reconsider the current technological culture, which is dependent on non-renewable fossil sources, to predominantly using long-term sustainable raw materials. Here, biorefineries based on wood and other lignocellulosics play a dominant role. One important process is sulphate cooking, where wood is separated into several fractions with varying values and applications (pulp, black liquor, etc.).

One of the smaller, but most valuable by-products (per tonne) is tall oil. The efficient recovery of tall oil can improve the economic and sustainability profile of the pulp and paper industry.

1.2 SCOPE

This project studied the solubility of the tall oil soap in black liquors, focusing on the ratio between fatty acids and rosin acids. In addition, the project investigated ways to manipulate the ratio between fatty acids and resin acids to reduce the solubility of the soap to enable improved saponification and thus achieve higher tall oil recovery.

1.3 IMPLEMENTATION

First, a methodology to study tall oil solubility in lab scale is developed based on established analytical methods and necessary modifications.

Next, synthetic liquors with defined mixtures of pure fatty acids and resin acids are prepared at different ratios and mixed with lignin, sodium hydroxide and sodium sulphide corresponding to typical black liquor composition and the tall oil solubility is investigated. From these well-defined mixtures, knowledge is obtained on the solubility of the tall oil.

Finally, the addition of fatty acids and rosin acids is tested in real samples of industrial black liquors to confirm the tall oil yield responses reported from the synthetic liquors.

From the results, strategies are suggested to improve the removal of tall oil in industrial kraft pulping liquors.

2 Technical background

2.1 WOOD CHEMISTRY

Wood consists mainly of the cell walls of cells in secondary xylem. Chemically, there are considerable differences between the different phylogenetic groups of plants. Technically, the differences between softwoods and hardwoods are the most important. The chemical component of wood used to be divided into five main groups: *cellulose, hemicellulose, lignin, extractives* and *inorganics*, where the three first components constitutes the material of *lignocellulose,* i.e., it is cellulose, hemicellulose and lignin that are responsible for the mechanical properties of wood; extractives and inorganic are components present in smaller amounts, that play minor structural roles, which does not imply that they are technically insignificant (Sjöström, 1993).
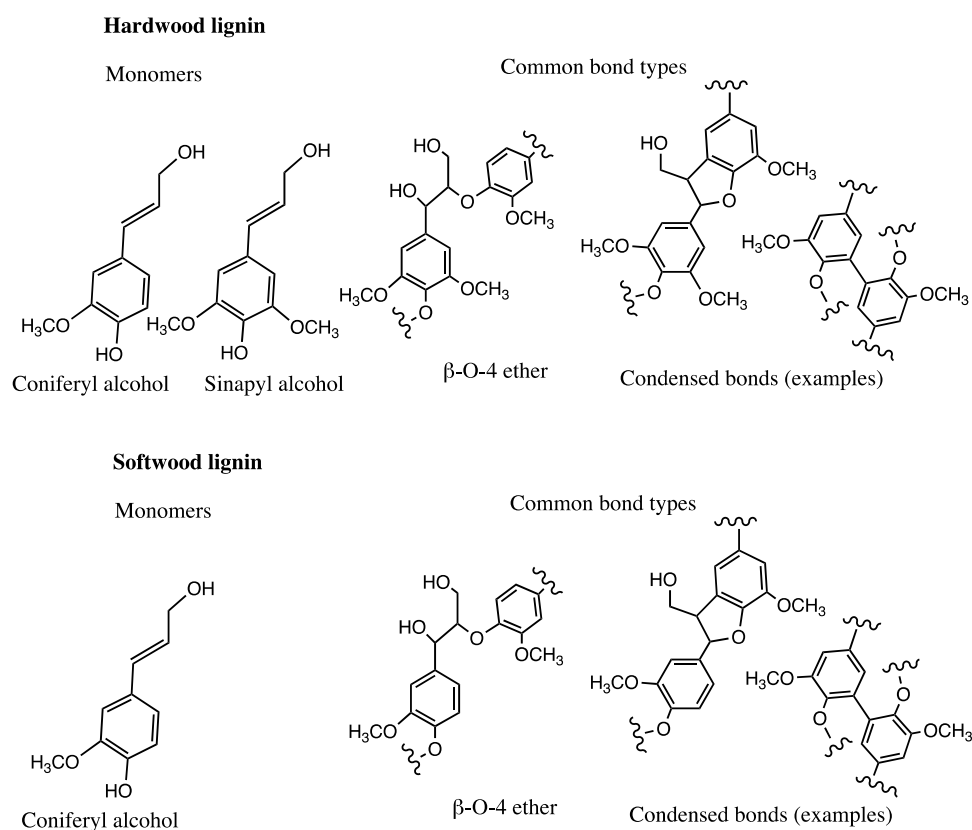

Figure 1. Differences between softwood and hardwood lignin. Hardwood lignin has a more complex monomer composition with more methoxy groups (-OCH₃). This leads to that the proportion of the relatively easy degraded beta-O-4 ether is higher in hardwood than in softwood lignin, which on the other hand has a higher content of stable condensed bonds.

While the cellulose is virtually the same in hardwoods and softwoods, there are considerable differences in the structure/composition of lignin and hemicelluloses; lignin in softwood consists almost entirely of coniferyl alcohol units, whereas the hardwood lignin consists of a mixture of conifer alcohol and sinapyl alcohol, i.e. hardwood lignin is more methoxylated than softwood lignin (Figure 1) (Ralph et al., 2004). A consequence of this is that the monomers in hardwood lignin will, to a larger extent, be connected by relatively easily degraded ethers and less stable carbon-carbon bonds than in softwood lignin. A technical result of this is that hardwood can be pulped faster and under milder conditions than softwood (Ragnar, Henriksson, Lindström, Wimby, & Süttinger, 2013).

The hemicelluloses are relatively short heteropolysaccharides that generally have side groups and chemical modifications, such as acetylations and methylations. In hardwood, glucuronoxylan is the dominating hemicellulose, with only a small contribution of glucomannan. In softwood, the galactoglucomannan is the most common with a significant minority of arabinoxylan (Carvalheiro, Duarte, & Girio, 2008). These differences are technically important since the mannan-based polysaccharides are degraded in kraft pulping to a much higher extent than xylan-based polysaccharides (Ragnar et al., 2013). The degradation products are also different. Both xylan and glucomannan form multiple covalent bonds to lignin ("lignin carbohydrate complexes" - LCC), that are obstacles for delignification in kraft pulping (Lawoko, Henriksson, & Gellerstedt, 2006).

The differences in lignin and hemicellulose are however small compared to the differences in the composition of extractives. The extractives are defined as low molecular weight (non-polymeric) organic components present in wood, where they can fulfil various functions, such as defence against invasion of micro-organisms (natural impregnation), or energy storage. Some extractives can also be chemical residues from the stage where the wood was formed. Not surprisingly, the extractives are a very heterogenic group, both structurally and physically. Some extractives are volatile and responsible for the characteristic smell of certain woods. Others are hydrophilic and water-soluble, whereas others are strongly hydrophobic or even amphiphilic. It is especially the latter that are interesting here – the most important ones are *fatty acids* that biologically mainly have played a role for energy storage as a part of triglycerides, but can also play other roles, and *rosin acids*, that mainly work as antimicrobial agents as part of the plant's defence system.

In Figure 2, examples of fatty acid and rosin acid structures are shown. The differences between wood species shall be underlined; hardwood generally contains no or little rosin acids and often less fatty acids than softwoods, among which pine has more amphiphilic extractives than spruce. Since the tall oil originates from these amphiphilic components, pine is the best raw material.

Example of fatty acids

Palmtoleic acid

Linoleic acid

Example of rosin acids

Abeic acid

Neoabeic acid
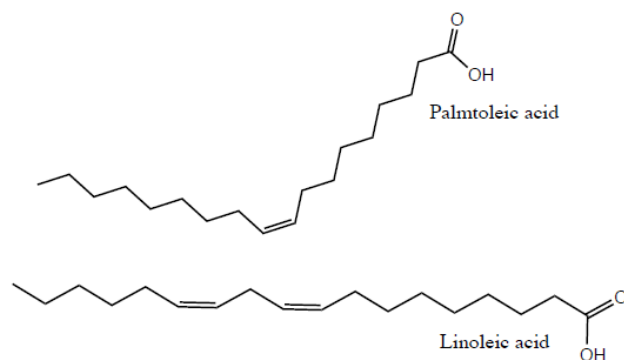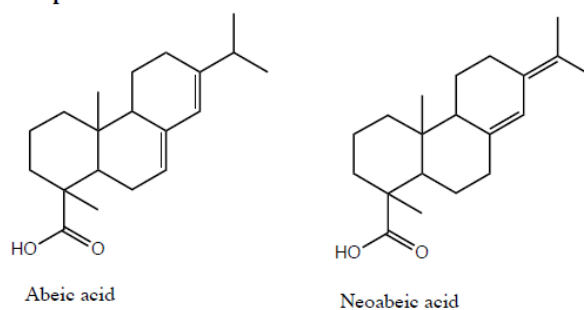
Figure 2. Examples of fatty acids and rosin acids. Although both groups are amphiphilic due to the carboxylic acid functionality, there are substantial differences, such as the fatty acids are much more flexible.

The main tall oil components are fatty acids (~45%), rosin acids (~42%), and unsaponifiable compounds (~13%) (Aro & Fatehi, 2017; Gunstone, 1996; Holmbom & Ekman, 1978). More specifically, tall oil fatty acids (TOFA) include primarily oleic (46%) and linoleic acid (41%), with smaller amounts of palmitic (5%), stearic (3%), linolenic (3%) and arachidic acids (2%) also present (Gunstone, 1996; Holmbom & Ekman, 1978). Tall oil rosin acids (TOR) are a mixture of abietic-type and pimaric-type acids, while unsaponifiables include various sterols, alcohols and aldehydes (Aro & Fatehi, 2017; Gunstone, 1996; Holmbom & Ekman, 1978).

The inorganic content of wood consists of various salts, of which calcium salts are the most common, but also potassium is a common cation. Unfortunately, wood also contains small amounts of heavy metals such as cadmium and chrome. The inorganic content of wood represents a problem since these salts will end up in the process liquors (Jenkins, Baxter, Miles, & Miles, 1998).

Energiforsk

2.2 KRAFT PULPING

Kraft pulping is for many years the dominating technique for the manufacture of chemical pulps from both hardwoods and softwoods, and is also by volume and produced value generally the largest pulping method. It consists of treatment of wood – normally in the form of wood chips – under high temperature and overpressure with white liquor – a solution of sodium hydroxide and sodium hydrogen sulfide. Under these conditions, the lignin is degraded by attacks in the most common bond in lignin – the beta-O-4 ether. (This explains why hardwood is easier to kraft pulp since its lignin has a higher content of beta-O-4 ethers that softwood lignin.) This degradation can be mainly of two types, one "slow sulphur independent" that can scissor the lignin "inside" a chain, and one "fast sulphur dependent" that cuts monomers "one-by-one" from the ends (Figure 3). Since the beta-O-4 bond is the most common bond in lignin and lignin oligomers have high solubility in alkali, it is not a major problem that the pulping cannot break the carbon-carbon bonds in lignin. Nevertheless, kraft puling does not continue until all lignin is removed, due to that unwanted side reactions create stable products, such as enol ethers. Covalent bonds between lignin and polysaccharides (LCC) are also an obstacle for complete delignification. The lignin fragments solubilized in the pulping liquor undergo a series of poorly following reactions that modify the structure producing strongly coloured components (Ragnar et al., 2013).

Slow sulphur independent scissoring delignification reaction

Fast sulphur dependent peeling delignification reaction
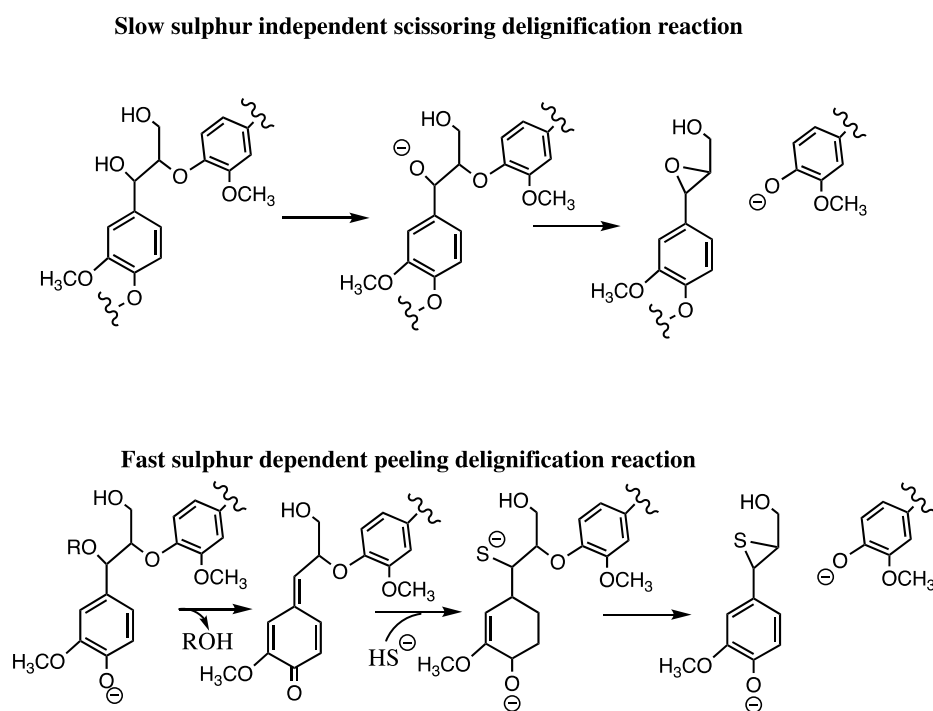
Figure 3. Important delignifying reactions in kraft pulping.

Also, the polysaccharides undergo chemical reactions during the kraft pulping, of which alkaline hydrolysis and peeling are the most important. However, different polysaccharides are having distinct sensitivity to these reactions, where cellulose generally is the most stable, and glucomannan and pectin the most sensitive. These reactions are generally unwanted since they lower the yield in pulping and often are negative for the strength properties of the pulp. The solubilized degradation products undergo – like lignin – a series of reactions in the pulping liquid and also strongly coloured pigments are formed.
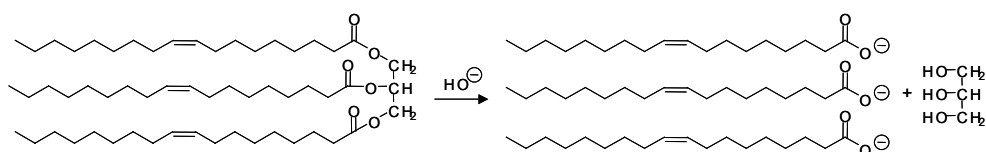
Figure 4. Hydrolysis of esters during kraft pulping forms fatty acids.

Many extractives are solubilized during the pulping, and also chemical reactions can occur – the most important is the hydrolysis of ester bonds for instance in triglycerides, which forms fatty acids (Figure 4). These are together with resin acids amphiphilic substances, and they can, therefore, work as "soap" in the pulping, solubilizing the most hydrophobic and poorly soluble extractives.

It is necessary for the efficiency of kraft pulping that a large excess of reaction chemicals (NaOH, NaSH) is present, i.e., very large amounts of chemicals are needed. Thus, it is essential both for economic and environmental reasons for kraft pulping to have a system for making the white liquor from the black liquor, i.e., a chemical recovery system.

2.3   CHEMICAL RECOVERY SYSTEM

The chemical recovery system that converts black liquor to white liquor is a totally necessary procedure for the kraft pulping and is a multi-stage procedure (Figure 5). The fact that the black liquor is an extremely complex mixture of inorganic and organic components makes the process complex. The inorganic components are remaining pulping chemicals (NaOH, NaSH), reaction products of these ($Na_2S_2O_3$, Na_2SO_4 etc.), and solubilized inorganics from the wood. The organic components are degradation products from lignin and polysaccharides and natural or chemically modified extractives. In Tables 1-3, some data of the composition of black liquor is listed. This will be discussed in more detail in the following sections. It shall also be underlined that the exact composition varies depending on the raw material, and it is especially important if the pulped wood is hardwood or softwood.
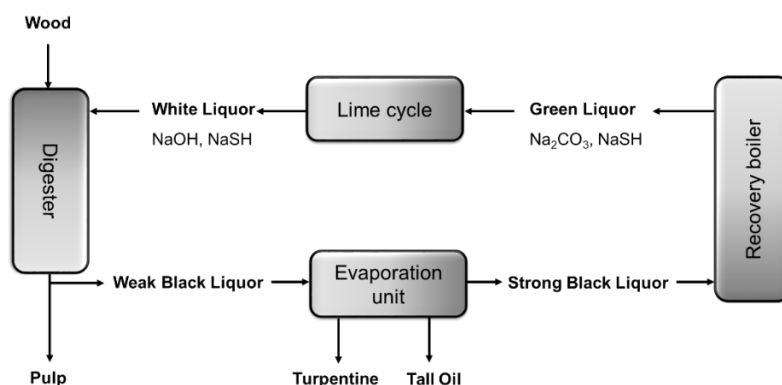
Figure 5. Stages in chemical recovery system.

The key step in the system is "limited combustion", i.e., burning with limited accessibility to oxygen, performed in the recovery boiler. However, the water content cannot be too high in the recovery boiler – a suitable dry content is 60-85%. Since the dry content in the original black liquor used to be around 15-18%, the black liquor needs to be concentrated. This is performed by exposure to a series of plates heated with steam that remove water as steam from the black liquor, and the produced steam can be "reused" for heating other plates, giving the process a relatively good energy economy. Together with the water, several volatile organic components are removed, which can be valuable by-products, such as methanol and raw turpentine, but also toxic and bad smelling components such as mercaptan and dimethyl sulfide. These components are often separated by distillation and the valuable by-products are taken care of, whereas mercaptan and dimethyl sulfide are transferred to the recovery boiler.

When the dry content is around 25-35%, tall oil can be removed from the black liquor using decantation as described below. In many cases, this stage is made more manually than the other part of the process that is highly automatized. The concentrated "strong" black liquor is sprayed in the recovery boiler where remaining water is vaporized, and the remaining solid undergoes a pyrolysis, that creates gases that can both be oxidized (CO_2, SO_2 etc.) and reduced (H_2, CO, H_2S etc.), salts (Na_2CO_3 etc.), and elementary carbon (char). Due to the construction of the recovery boiler, where oxygen is added in excess in the upper part and is very limited in the lower part, the chemical conditions will be different in the upper part that is oxidizing burning reducing gases, generating a large excess of heat. Sodium gases react with sulfur dioxide forming sodium sulfate that can be recovered from the smoke gas and returned to the black liquor. In the lower part, on the other side, elementary carbon and reducing gases create a reducing atmosphere that reduces sulfur containing chemicals to sulfides. Thus, a salt melt will be formed in the recovery boiler that contains Na_2CO_3 and Na_2S contaminated with char and various types of contaminating salts – mainly carbonates.

The smelt is leaked out from the bottom of the recovery boiler and dissolved in water forming the green liquor, followed by a filtration that removes char and most of the contaminating salts. The green liquor is converted into white liquor by treatment with CaO. A by-product of this is $CaCO_3$ that is converted to CaO in a lime kiln (Reeve, 2002).

2.4 BLACK LIQUOR COMPOSITION

The spent liquors from industrial kraft pulping contain hundreds of organic compounds originating from all wood constituents (e.g. lignin, hemicellulose, tall oil, etc.), in addition to the inorganic cooking chemicals and their derivatives (Aro & Fatehi, 2017; Niemelä & Alén, 1999). A typical composition of black liquors from kraft pulping of pine and birch wood is presented in Table 1. The main differences between these common black liquors are the slightly lower (about 20% less) lignin content and the presence of 3.5 times more residual polysaccharides, mainly xylan in birch black liquors compared to ones from pine (Table 1).

Table 1. Typical composition (% of dry matter) of kraft black liquor during pulping of pine and birch wood (Niemelä & Alén, 1999).

Component	Pine	Birch
Lignin	31	25
High molecular weight (>500 Da) fraction	28	22
Low molecular weight (<500 Da) fraction	3	3
Aliphatic carboxylic acids	29	31
Formic acid	6	4
Acetic acid	4	8
Other carboxylic acids (non-volatile, polar)	19	19
Other organics	7	11
Extractives	4	3
Polysaccharides	2	7
Miscellaneous	1	1
Inorganics	33	33
Sodium bound to organics	11	11
Inorganic compounds	22	22

The inorganic salts present in black liquors are shown in Table 2 and include the kraft cooking chemicals and their derivatives, such as NaOH, Na_2S, Na_2CO_3 and other Na salts of oxidized sulfur ions (Niemelä & Alén, 1999).

Table 2. Typical content of inorganic salts in pine kraft black liquor (Niemelä & Alén, 1999).

Inorganics	% of inorganics
NaOH	6
Na_2S	17
Na_2CO_3	32
Na_2SO_3	7
Na_2SO_4	12
$Na_2S_2O_3$	14
Others (K salts, chlorides, etc.)	12

Table 3 provides a detailed list of the numerous aliphatic carboxylic acids (non-volatile polar mono- and di-carboxylic acids) formed when wood components are decomposed by the cooking chemicals and harsh pulping conditions (Niemelä &

Alén, 1999). All of these compounds have been detected in kraft black liquors from pine, birch and eucalyptus wood pulping, with some variations especially in the amount of xyloisosaccharinic and glucoisosaccharinic acids, which can be attributed to the difference in their composition in polysaccharides that they derive from.

Table 3. Main non-volatile polar carboxylic acids (>0.10 g/L) in kraft black liquors of common softwood and hardwood species (Niemelä & Alén, 1999).

Monocarboxylic acids	Pine (softwood)	Birch (hardwood)	Eucalyptus (hardwood)
Glycolic	2.54	2.31	1.99
Lactic	4.20	3.83	2.65
Glyceric	0.13	0.11	0.08
2-Hydroxybutanoic	1.04	6.82	2.95
4-Hydroxybutanoic	0.19	0.10	0.08
3-Deoxytetronic	0.26	0.59	0.36
2-Hydroxypentenoic	0.30	0.15	0.16
3,4-Dideoxypentonic	2.25	1.18	1.21
3-Deoxypentonic [a]	1.46	0.88	0.81
Xyloisosaccharinic	0.48	3.76	1.90
Anhydroisosaccharinic [a]	0.34	0.18	0.13
3,6-Dideoxyhexonic [b]	0.16	0.56	0.29
3-Deoxyhexonic [c]	0.30	0.30	0.18
Glucoisosaccharinic [a]	8.97	4.11	3.48
Dicarboxylic acids			
Oxalic	0.13	0.17	0.42
Succinic	0.22	0.22	0.33
Methylsuccinic	0.18	0.04	0.16
Malic	0.16	0.27	0.19
2-Hydroxyglutaric	0.39	0.50	0.66
2-Hydroxyadipic	0.43	0.24	0.12
2,5-Dihydroxyadipic [a]	0.42	0.22	0.28
Glucoisosaccharinaric [a]	0.47	0.69	0.59

[a] erythro and threo isomers.

[b] ribo and arabino isomers.

[c] ribo, arabino, xylo, and lyxo isomers.

2.5 COMMERCIAL TALL OIL PRODUCTION PROCESS

Tall oil production, as discussed above, is typically integrated into the chemical recovery system of the kraft pulping process and can be divided into three sections: (1) separation of tall oil soap; (2) conversion of tall oil soap into crude tall oil; (3) purification and fractionation of crude tall oil (Aro & Fatehi, 2017; Huibers, 2000; Wansbrough, Rough, & Cooney, 2017).

2.5.1 Separation of tall oil soap

The highly alkaline environment in the kraft pulping process leads to the formation of soluble sodium salts of tall oil fatty and rosin acids, known as tall oil soap, as well as sodium salts of lignin and other wood components found in black liquor (Aro & Fatehi, 2017). The main factors that influence soap formation are the type of wood species, solids concentration, cooking temperature, and residual effective alkalinity (Foran, 1992).

The black liquor has a typical concentration of 15 % (w/w), in which the tall oil soap remains soluble. When its solid concentration further increases, the soap becomes insoluble due to common ion effect and can be removed via settling or skimming. However, if the black liquor becomes too dense, and hence more viscous, then the soap recovery greatly diminishes. Typically, the black liquor is concentrated to 20-30 wt.% for optimum tall oil soap recovery (Aro & Fatehi, 2017; Foran, 1992). The insoluble part of the tall oil soap forms micelles that aggregate and flow up on the surface of the black liquor, where they are separated (skimmed off or decanted) and transferred into a storage tank for the next step in the process (Aro & Fatehi, 2017). Various designs of skimming apparatus ('skimmers') with different efficiencies have been proposed and used by the mills. The soap rising rate and residence time, the black liquor downdraft (superficial velocity), skimmer baffling, liquor level control, and soap bed depth are among the main factors affecting the skimming efficiency by the skimmers (Foran, 1992).

Unfortunately, up to 20-40% of tall oil soap still remains soluble in the black liquor and cannot be recovered (Aro & Fatehi, 2017). Therefore, studying the solubility of tall oil in black liquor is of great importance to find ways that improve the overall efficiency of tall oil production, as discussed in the following sections.

2.5.2 Conversion of tall oil soap into crude tall oil

Crude tall oil (CTO) is produced by reacting the skimmed tall oil soap with a strong acid, typically 90-95% sulfuric acid. The sodium salts of fatty and rosin acids (soap) are converted into their respective free carboxylic acid forms, as depicted in the following chemical equation (Aro & Fatehi, 2017):

$$R - COO^- Na^+ \; + \; H^+ \; \rightarrow \; R - COOH \; + \; Na^+$$
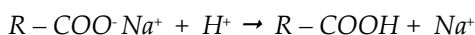
This reaction is known as acidulation and involves heating of the soap to boiling point (for 2 h) using steam and then adding the acid to reach pH about 3-4 (batch mode) or diluting continuously with water and reacting with dilute sulfuric acid (continuous mode) (Aro & Fatehi, 2017; Huibers, 2000). The formed CTO is the lightest component and collects on the top phase of the reactor. In the batch mode,

the mixture is left overnight to settle before the separation of the three distinct phases (lighter to heavier): CTO, lignin (insoluble and emulsion) and the aqueous phase with the spent acid. CTO is pumped out and sent for further processing, while lignin is sent back to the recovery cycle of the kraft pulping process as an energy source and spent acid is returned to the initial soap storage tank for treatment of the tall oil soap (Aro & Fatehi, 2017; Huibers, 2000).

2.5.3 Fractionation and purification of crude tall oil

The recovered CTO can be sold as it is or further fractionated and purified depending on the desired application and market opportunities. Five different products can be separated from the distillation of CTO based on volatility differences during continuous evaporation and distillation process steps (Aro & Fatehi, 2017):

1. volatile (light) products, known as 'heads' (during the initial evaporation step),
2. pitch (heavy part of the initial evaporation step),
3. tall oil rosin acids (TOR, bottom stream after the first distillation of evaporation stream),
4. tall oil fatty acids (TOFA, overhead stream after the final distillation),
5. distilled tall oil (DTO, bottom stream after the final distillation).

An alternative but not very common route of purifying CTO without complete fractionation includes its dissolving in naphtha, mixing with sulfuric acid, washing, neutralizing and finally steam stripping. The profile of the resulting product (e.g. color, odor, viscosity) varies depending on the reaction conditions and end uses (Aro & Fatehi, 2017).

2.6 USES OF TALL OIL

Tall oil is one of the commercially viable by-products of the kraft pulping process. In 2006, it has been reported that 1.6 million metric tons per year were produced globally, and the tall oil production is expected to reach 2 million in 2018 (Aro & Fatehi, 2017). Crude tall oil as well as all 5 products from its fractionation, namely TOFA, TOR, pitch, heads, and DTO, have commercial uses and applications.

2.6.1 TOFA and TOR

The market for TOFA is greater than the rest of the products from tall oil distillation and the purity of produced TOFA can be very high (90-98%) (Aro & Fatehi, 2017). They are used commercially in the production of coatings, inks, and adhesives, as chemical intermediates, in the production soap and detergent, as well as flotation aids in mining and polishes in metalworking (Aro & Fatehi, 2017; Huibers, 2000; Wang, 2018; Wansbrough et al., 2017). The purity of produced TOR is also very high (90-95%), but typically require to be mixed with alcohols to improve their solubility and further chemical processing (hydrogenation and polymerization) to be converted to end products such as rubbers, electronics, papermaking, coatings, and inks. (Aro & Fatehi, 2017; Huibers, 2000; Wang, 2018; Wansbrough et al., 2017).

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Novel potential applications of TOFA and TOR have also been developed and include ionic liquids and flame-retardants (Wang, 2018), as well as the production of biofuels such as renewable hydrocarbons (Jenab, Mussone, Nam, & Bressler, 2014) and biodiesel (Demirbas, 2008).

2.6.2   Pitch and heads

Various sterols (e.g. phytosterols and phytostanols) and rubber softeners can be produced from the pitch, or used as a constituent of drilling mud (Aro & Fatehi, 2017). The heads have uses as lubricants, corrosion inhibitors or burned as fuel and when combined with the pitch part they form asphalt fluid for road construction (Aro & Fatehi, 2017; Huibers, 2000).

2.7   HOW TO IMPROVE TALL OIL SOAP RECOVERY

Since the tall oil is a by-product and not the main product of the process, the possibilities to optimize the conditions for maximal tall oil production are limited. However, there are yet several possible efforts that can be made, such as *choice of dry content* in the black liquor, *temperature*, and *additions* as long as they do not disturb the chemical recovery system.

2.7.1   Factors affecting soap solubility in black liquor

It is already known that the solid content of the black liquor and temperature have a major impact on the solubility of the tall oil soap (Foran, 1992; Nordenö, 2008). The solubility of tall oil soap is greater in the weak black liquor (about 15% solids) and lower in the intermediate black liquor (20-30% solids) (Foran, 1992). At higher solid content the black liquor becomes too viscous, rendering the soap recovery extremely difficult (Aro & Fatehi, 2017). High temperatures (above 80°C) seem to promote tall oil soap solubility (Foran, 1992), which means that cooling the black liquor down to below 80°C could improve soap separation. However, the temperature and solid content of the black liquor are typically fixed by the operating conditions of the mill and difficult and costly to change. In addition, the viscosity of black liquor generally increases greatly as temperature drops. Therefore, lowering the liquor temperature would not necessarily improve the efficiency of soap recovery (Foran, 1992).

It has been previously described that soap separation is influenced by temperature, tank design, residual effective alkali content, addition of air, ratio of fatty acids to rosin acids (Foran, 1992), addition of air (Tran, 2011), ratio of fatty acids to rosin acids (Foran, 1992), and blending of hardwood-softwood liquors (Foran, 1992).

2.7.2   Tall oil yield and cause of losses

The wood species, harvest season, and wood storage practices affect considerably the available amount of tall oil to be recovered, which also varies between pulp mills due to different practices in storage and operation (Foran, 1992). The yield of recovered CTO ranges from 15-50 kg tall oil per ton of pulp, which indicates a range of 45-75% of the tall oil in the pine wood that can be recovered (Aro &

Fatehi, 2017; Huibers, 2000; Wansbrough et al., 2017). The CTO losses can be attributed to all process steps in wood pulping (Huibers, 2000):

- wood cutting and storage operations,
- wood pulping,
- soap recovery from black liquor, and
- soap acidulation into CTO.

Many improvements have been applied and novel ones have been suggested to improve the tall oil yield, as discussed in the following sections.

2.7.3 Improving soap recovery efficiency

Various improvements have been proposed and applied to improve the tall oil yield in each process step in kraft pulp mills. Studies in Swedish mills by Värmeforsk (Johansson, 2007; Nordenö, 2008) revealed a potential to increase tall oil production by more than 10%, or 30 000 tons per year.

Wood cutting and storage operations

Wood cutting and storage operations have become more efficient, improving turnover rates over the years from two months to one week (Huibers, 2000), which reduces tall oil losses from wood decomposition. A study in Swedish mills by Värmeforsk (Johansson, 2007) revealed that the species of wood and the place the trees grew are more significant than wood storing, but these factors are difficult to manipulate. A later study by Värmeforsk (Nordenö, 2008) reported that higher moisture content in the wood leads to higher tall oil yield, either due to its effect in wood storage or due to seasonal variation of wood composition.

Wood pulping

During wood pulping a portion of tall oil soap is adsorbed on the pulp, which can be recovered by the addition of chemicals to the pulp wash water, such as *N,N*-dimethyl amide or propyl stearic amide (Huibers, 2000).

Soap recovery from black liquor (skimming)

As discussed previously, optimizing the efficiency of the skimmer (in terms of starting solid content, baffling, level control, and soap bed depth) is an important way of improving overall tall oil soap recovery (Foran, 1992; Huibers, 2000).

In addition, other methods have been proposed or demonstrated that can further improve soap recovery and include air injection, electro-flocculation, the addition of chemicals, and alkaline washing (Aro & Fatehi, 2017; Foran, 1992; Huibers, 2000). Injecting fine bubbles of air at an optimum of 7.5 L/m^3 can be a simple and low-cost method to improve skimming efficiency (Foran, 1992; Tran, 2011). Electro-flocculation can be achieved by applying an electrical field to the black liquor stream, causing soap particles to agglomerate into larger particles that separate more easily (Foran, 1992). Proprietary commercial chemicals (surfactants) added in the black liquor have been reported to improved soap recovery at low dosages (Foran, 1992). Polymer addition may increase the soap separation rate, viscosity and purity, but may negatively affect the following step of soap acidulation (Aro &

Fatehi, 2017). However, the presence of the polymer polyoxypropylene-polyoxyethylene in black liquor has been reported to have improved the soap recovery from 58% to 70% (Ziegler & Lieberman, 1975).

The recycling of tall oil components back into the process stream has also been proposed to improve tall oil soap separation, without affecting considerably the process or increasing the production cost. For example, adding a small amount (0.01-0.04%) of beta-sitosterol, a by-product from tall oil production, has been shown to improve tall oil yields by 10% (Aro & Fatehi, 2017). As the ratio between fatty acids and resin acids seems to be an important parameter in tall oil solubility (Foran, 1992; Uloth, Shewchuk, Guy, & van Heek, 2009), where a higher ratio leads to lower solubility, one suggestion to reduce tall oil soap solubility (and increase soap separation) is by adding fatty acids into the separation stream. Uloth et al. (2009) have demonstrated that adding waste fatty acids to black liquor decreased tall oil soap solubility and hence increased the efficiency of soap skimming in kraft pulp mills. Fatty acids can be obtained from refined tall oil, but also from other sources of vegetable oil, such as rapeseed, or from tall oil originating from other species of wood.

As discussed previously, the solubility of tall oil soap decreases as the black liquor gets concentrated (Foran, 1992), which enables more insoluble soap to rise to the top and be skimmed. However, if black liquor becomes too dense then the recovery of soap diminishes due to the high viscosity of the liquor (Aro & Fatehi, 2017). In addition, the ionic strength of the liquor greatly affects the solubility of fatty acids and rosin acids (Björklund Jansson & Nilvebrant, 2009). Therefore, one possible way to generate more insoluble soap, and hence improve the tall oil recovery yields, would be to increase only the ionic strength and not the solids (that make the liquid more viscous). This is not a simple matter since one cannot simply add external salts to the black liquor because this can influence the chemical recovery system in a negative way. However, there are possibilities to generate salts "internally" in the mill: one possibility is to concentrate white liquor and add it to the black liquor; another is to do the same thing with green liquor; and a third possibility is to use the Na_2SO_4 obtained from the fly ash from the recovery boiler.

Soap acidulation step

CTO yield during the acidulation step can be improved by the addition of dispersants, such as commercial lignosulphonates, which promote the aggregation of the reverse fatty and rosin acid micelles formed after neutralization of their respective sodium salts (Huibers, 2000). However, according to the study in Swedish pulp mills by Värmeforsk, the efficiency of soap recovery from the black liquor (i.e. before acidulation step) is far more important than the de-soaping step (acidulation), which can be adjusted without significant cost (Johansson, 2007).

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2.8 EXPERIMENTAL CHALLENGES IN STUDYING TALL OIL SOLUBILITY

2.8.1 Working with real industrial liquors

Studying the solubility of tall oil soap in real industrial black liquor samples poses many challenges, such as significant compositional variations due to differences in the wood chip feedstock as described in the previous sections. In addition, there are practical issues in collecting representable samples from the pulp mill tanks, as well as preparing aliquots (splitting the sample) with identical composition (Saltsman & Kuiken, 1959) for correctly studying the effect of multiple factors on the solubility of tall oil soap. Therefore, a synthetic liquor that simulates the industrial black liquor from kraft pulping of pine wood was necessary to be established in the lab to study the tall oil solubility.

2.8.2 Tall oil soap analytical challenges

Conventional procedures for the analysis of tall oil generally involve an extraction step, which separates the tall oil from the black liquor or other process streams. This separation typically is done by solvent extraction (Saltsman & Kuiken, 1959; Voss & Rapsomatiotis, 1985; Wilson, 1971), or solid phase extraction (Backa, Brolin, & Nilvebrant, 1989; Rogers & Mahood, 1977; Sweeney, 1988) to yield the total extractives after evaporation of the solvent.

The choice of the isolation method is important because it may limit the maximum recovery of the compounds of interest and may lead to co-extractives that can interfere with the analysis (Voss & Rapsomatiotis, 1985). The use of solid phase extraction of tall oil fatty and rosin acids from pulp mill effluents by adsorption onto a porous polymeric resin was recommended mostly for qualitative analyses and for studies involving processing of large sample volumes (Voss & Rapsomatiotis, 1985). In principle, organic solvent extraction should provide a simple method of isolation of tall oil for black liquor. However, solvent extraction of pulp mill effluents is time-consuming and is associated with issues such as the formation of foaming emulsions, making the analysis of tall oil difficult and may lead to low recoveries and poor reproducibility (Voss & Rapsomatiotis, 1985).

The accurate characterization of tall oil extractives can be performed using gas or liquid chromatography (Voss & Rapsomatiotis, 1985). However, these procedures are time-consuming and require the use of sophisticated and expensive analytical instruments not typically available in mills (Sithole, 1993), as well as specialized technical personnel to do the analysis.

The above analytical challenges add to the lack of knowledge of the tall oil solubility in the black liquors and its soap separation.

2.9 ANALYTICAL METHODS FOR DETERMINATION OF TALL OIL CONTENT

Common analytical methods and standard protocols described in the literature for the estimation of tall oil in pulp and paper industry process streams are presented in brief in the following paragraphs.

2.9.1 Solvent extraction and simple gravimetric estimation

Saltsman and Kuiken, TAPPI Journal, 1959

One method commonly referenced in tall oil literature is the one developed by Saltsman and Kuiken (1959), which involves liquor dilution to about 5% solids, followed by multiple steps of acidification and extraction with acetone-methanol-petroleum ether, evaporation of the extracted solvent, drying and gravimetric estimation of the extracted tall oil.

Wilson, Svensk Papperstidning, 1971

This method developed by Wilson (1971) uses trichloroethylene as the organic solvent to extract the tall oil from black liquor, followed by acidification, evaporation of the solvent phase and gravimetric determination of the extracted tall oil.

2.9.2 Solvent extraction and titration with dye

PCTM 24, Pine Chemicals Association, 1996

The PCTM 24 standard "method of estimating crude tall oil (CTO) in black liquor" by the Pine Chemicals Association (1996) is a modification of the Saltsman and Kuiken (1959) method. The difference here is that the extracted tall oil is re-dissolved (in isopropyl alcohol) and titrated with KOH using a dye indicator solution (phenolphthalein), instead of gravimetric analysis. Tall oil is calculated based on the amount of KOH added and the acid number of the oil.

2.9.3 One-step solvent extraction

Voss and Rapsomatiotis, Journal of Chromatography, 1985

A method developed by Voss and Rapsomatiotis (1985) involves the isolation of tall oil fatty and rosin acids in pull mill effluents by a 1-step extraction with an equal volume of methyl *t*-butyl ether (MTBE) in alkaline conditions (pH 9). These conditions are reported to overcome some of the issues encountered during solvent extraction of pulp mill effluents, such as the formation of emulsions, precipitation of lignin, and isomerization of rosin acids (Voss & Rapsomatiotis, 1985). Finally, the extracted tall oil undergoes chemical transformation (methylation), and the methylated extract is analyzed by gas chromatography.

2.9.4 Spectrophotometric analysis of extracted tall oil

Sitholé, TAPPI Journal, 1993

Sithole (1993) has adapted a rapid colorimetric procedure for measuring free fatty acids in vegetable oils (Baker, 1964) to be used for the determination of total free fatty and resin acids in extractives from pulp and paper samples. However, the tall oil would need to be first extracted from the black liquor into a suitable organic solvent. Then, the extracted fatty and resin acids are complexed with cupric ions, extracted into another solvent and their concentration is measured colorimetrically using a common spectrophotometer.

The applicability of this method has been demonstrated in various samples from pulp mills, including pitch deposits, wood chips, white waters, and other effluents, and its results are in agreement with more sophisticated chromatographic determinations (Sithole, 1993). However, to our knowledge, it has not been previously reported in black liquor extractives, so some testing and optimization were necessary to be used in the present tall oil solubility study.

3 Materials and methods

3.1 DEFINITION OF THE SYNTHETIC BLACK LIQUOR

Preparing a synthetic liquor that includes the hundreds of compounds shown in Tables 1-3 (Materials and Methods section) can be considered impractical for the purposes of the present tall oil solubility study. Therefore, only the main components that may affect the tall oil solubility were chosen. More specifically, the carboxylic acids shown in Table 3 were substituted by lactic acid (one of the main acids formed and commercially available) on the same molar basis. Xylan was selected to be the main polysaccharide fraction in the synthetic liquor since it is the dominating polysaccharide after kraft pulp cooking (Niemelä & Alén, 1999). The defined simplified synthetic liquor that adequately simulates the industrial black liquors for the present tall oil solubility study is shown in Table 4.

In pulp mills, tall oil soap is collected (skimmed) after concentrating the 'weak' black liquor (15% w/v total solids) to above 25% (w/v) total solids. Therefore, the composition of the simplified black liquor was adjusted accordingly (Table 4) for the solubility experiments to better resemble the industrial tall oil soap skimming conditions. All compounds in Table 4 were available or procured at sufficient amounts for the present study.

Table 4. Composition of defined black liquors used in the present study. Preliminary tests and the study of the effect of fatty to rosin acid ratio included only inorganic salts and tall oil. Lignin was further added to study its effect on tall oil solubility. Full synthetic liquors (all components in the table) were only prepared to verify the performance of the developed tall oil analytical procedure.

Component type	Specific compound	% of solids in black liquors	g/L at 15% solids	g/L at 25% solids
Lignin	kraft lignin	31	47	78
	formic acid	6	9	15
Aliphatic carboxylic acids	acetic acid	4	6	10
	lactic acid (as non-volatile polar carboxylic acids, molar base)	11	17	28
Other organics	tall oil rosin and fatty acids	4	6	10
	xylan (as main polysaccharide)	2	3	5
	NaOH	2	3	5
	Na_2S	6	8	14
Inorganic salts	Na_2CO_3	11	16	26
	Na_2SO_3	2	3	6
	Na_2SO_4	4	6	10
	$Na_2S_2O_3$	5	7	12

3.2 DEVELOPED PROTOCOL FOR STUDYING TALL OIL SOLUBILITY

The developed experimental procedure for studying the tall oil solubility can be summarized in four parts: (A) preparation of synthetic black liquor; (B) soap skimming; (C) tall oil soap extraction; (D) tall oil estimation. Details on each part are presented in the following sections.

A. Preparation of full synthetic black liquor

First, prepare stock solutions of:

1. Inorganic sodium salts (2.5x concentrated) in deionized water:
   - × NaOH   5.0 g/L
   - × Na_2S 14.0 g/L (or 43.1 g/L of $Na_2S \cdot 9\,H_2O$)
   - × Na_2CO_3 26.4 g/L
   - × Na_2SO_3 5.8 g/L
   - × Na_2SO_4 9.9 g/L
   - × $Na_2S_2O_3$ 11.6 g/L

2. Organic acids mix (10x concentrated) in deionized water:
   - × Formic acid   15.0 g/L
   - × Acetic acid   10.0 g/L
   - × Lactic acid   27.5 g/L

3. Xylan (5x concentrated) in deionized water:
   - × Purified xylan   5.0 g/L

4. Tall oil fatty acids (TOFA, 10x concentrated) in acetone:
   - × TOFA   5.0 g/L

5. Tall oil rosin acids (10x concentrated) in acetone
   - × TOR   5.0 g/L

Next, prepare synthetic black liquor samples of 5 mL final volume in 15-mL screw cap test tubes (preferably glass):

- Mix the required amount of TOFA and TOR, stock solutions 4 and 5, respectively into a 15-mL test tube with screw cap. E.g. to make a TOFA-TOR ratio of 1 add 0.5 mL of each stock solution.
- Evaporate completely the acetone in the tubes (using a warm bath or air dry) before adding the other components.
- Weigh 0.40 g (dry weight) of lignin (e.g. Lignoboost lignin) in each tube.
- Add 1.2 mL of deionized water in each tube.
- Add 2 mL of inorganic salts mix (solution 1).
- Add 0.5 mL of organic acids mix (solution 2).
- Add 1 mL of xylan stock (solution 3).
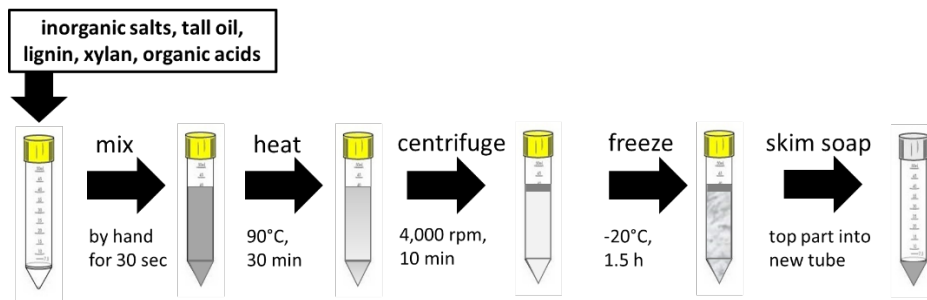- Mix gently to avoid excessive foam formation.

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Figure 6. Experimental steps for synthetic black liquor preparation and soap skimming.

B. Soap skimming (Figure 6)

- Incubate the synthetic liquor tubes at 90°C for 30 min.
- Centrifuge at 4 000 rpm for 10 min.
- Mark tube right below soap pellet (if not visible then mark at 90% of liquor volume, i.e. 4.5 mL).
- Cool-down and store at 4°C for 24 h.
- Freeze for 2-3 h at -20°C.
- Skim soap by transferring the frozen part above the marked line into a new 50-mL tube.

C. Tall oil soap extraction (Figure 7)

- Add 0.2 mL of 1M H_2SO_4 to each skimmed soap sample to reduce the pH to 10-11 (from 13+).
- Add 4 mL of 0.2 M pH 9 carbonate buffer to adjust pH around 9 (avoid immersing a pH probe due to potential losses of tall oil soap sticking on the probe).
- Extract twice the tall oil with 10mL methyl *t*-butyl ether (MTBE).
- Combine the two extractives into a new test tube (at least 15-mL, preferably 50-mL that have wider opening for faster evaporation).
- Evaporate the solvent by placing the tubes in a warm bath (40°C, not higher as MTBE will boil and material could spill out and be lost).
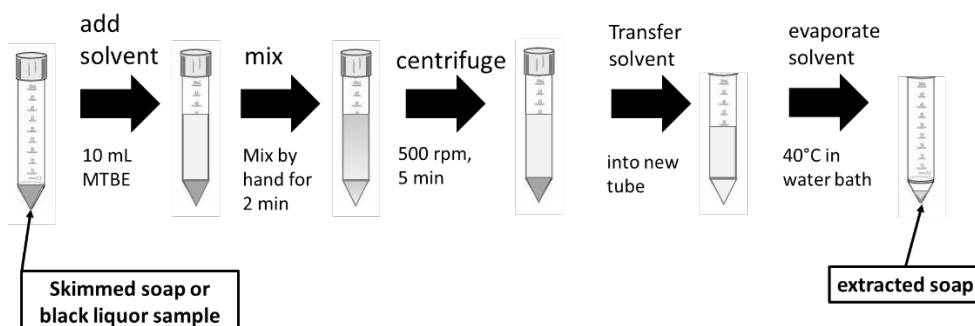

Figure 7. Experimental steps for tall oil soap extraction.

D. Tall oil estimation by colorimetry (Figure 8)

- Re-dissolve the dried tall oil soap sample in 2 mL acetone.
- Prepare a 'blank' sample with only 2 mL acetone.
- Prepare a fresh standard sample of tall oil fatty acids (weigh about 20 mg, record weight) and dissolve in 2 mL acetone.
- Add 3 mL of 5% (w/v) copper (II) acetate solution to all tubes.
- Add 5 mL hexane to all tubes.
- Mix thoroughly for 2 min.
- Centrifuge tubes at 500 rpm for 5 min to separate phases.
- Measure the absorbance of the hexane (top) phase at 677 nm (tall oil) and subtract the absorbance at 497 nm (baseline).
- Calculate the amount of tall oil (fatty acids equivalents) using a calibration curve (see following section) and normalizing with absorbance of the freshly prepared tall oil fatty acids standard sample.
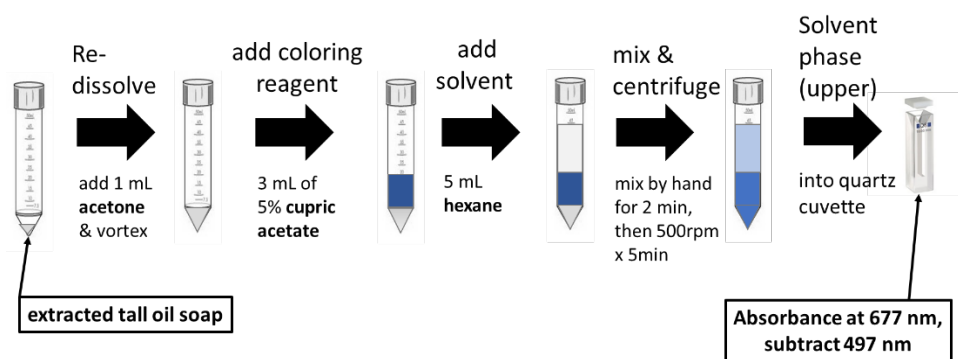
Figure 8. Experimental steps for tall oil colorimetric estimation.

3.3 EQUIPMENT

Oven drying was conducted in a drying and heating chamber (Binder, Germany). Rotofix 32A centrifuge (Hettich, Germany) was used for centrifuging black liquor and extracted tall oil samples up to 4,000 rpm. The colorimetric analysis was performed in a UV-2550 spectrophotometer (Shimadzu, Japan). A SevenCompact pH meter (Mettler-Toledo, U.S.A.) was used for pH measurements.

3.4   COLORIMETRIC METHOD CALIBRATION

Standard solutions of 0 – 30 mg of tall oil fatty acids, rosin acids and oleic acid (for comparison and to be used as proxy) were prepared in acetone and analyzed according to the colorimetric method by (Sithole, 1993), as summarized in section 0. The standard curves and linear correlation equations (R^2 in the range of 0.97 – 0.98) for tall oil fatty acids, rosin acids and oleic acid are presented in Figure 9 and Equations 1-3, respectively. The correlation coefficient of tall oil fatty acids was found lower than rosin acids, but very similar to oleic acid, which was expected as oleic is the main fatty acid (46%) of tall oil (Gunstone, 1996; Holmbom & Ekman, 1978).
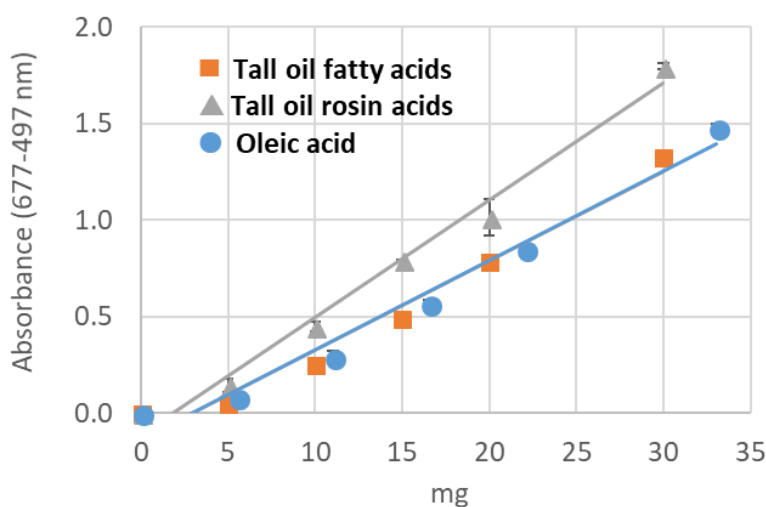
Figure 9. Calibration curves of tall oil fatty acids, rosin acids, and oleic acid using the colorimetric method by Sithole (1993).

Tall oil fatty acids

Absorbance $_{(677\text{-}497\ nm)}$ = 0.0460 * mg – 0.1302   **Eq. 1**

Tall oil rosin acids

Absorbance $_{(677\text{-}497\ nm)}$ = 0.0605 * mg – 0.1074   **Eq. 2**

Oleic acid

Absorbance $_{(677\text{-}497\ nm)}$ = 0.0461 * mg – 0.1312   **Eq. 3**

3.5 TALL OIL RECOVERY CALCULATION

The tall oil soap recovery % (*SR*) was calculated from the gravimetric or the colorimetric analysis based on the following equation:

$$SR\ (\%) = \frac{mg\ of\ estimated\ tall\ oil}{mg\ of\ total\ tall\ oil\ in\ black\ liquor} \qquad \textbf{Eq. 4}$$

Tall oil soap recovery % (*SR*) could be efficiently described by a logistic model (Eq. 5), using the ratio (r) of fatty acids to rosin acids present in the synthetic liquor:

$$SR(r) = SR_0 + \frac{SR_{max}}{1+e^{-k(r-r_m)}} \qquad \textbf{Eq. 5}$$

where *S* is the tall oil soap yield (%, dry weight basis), *r* is the ratio of fatty acids to rosin acids (by weight), *k* is a constant that determines the curvature of the model, r_m is the inflection point at which the yield increase rate reaches its maximum value.

3.6 MATERIALS

All chemicals used in the present study (inorganic sodium salts, extraction solvents, organic acids, and colorimetry reagents) were of analytical grade or greater. Purified tall oil fatty acids and rosin acids were generously provided by SunPine AB (Piteå, Sweden). Lignoboost lignin was used as the lignin fraction in kraft black liquor, while xylan purified from eucalyptus was used as the main polysaccharide fraction.

Industrial black liquors were kindly provided by Södra Skogsägarna and Svenska Cellulosa Aktiebolaget (SCA) and stored at 4°C until further processing and analysis:

a) 2 liters of black liquor from a pulp mill by Södra with 18.9% dry matter (as reported by the mill).

b) 2 liters of intermediate ("blandlut") black liquor from Obbola pulp mill (SCA) with approximately 21% dry matter (as reported by the mill).

3.7 TALL OIL FATTY ACID AND ROSIN ACID ANALYSIS IN INDUSTRIAL BLACK LIQUORS

The analysis of the fatty acid and rosin acid content of the received industrial black liquors from Södra and Obbola pulp mills was conducted by MoRe Research (Örnsköldsvik, Sweden) using the GC-Åbo method.

4   Developing a 'model system' to study tall oil solubility

In the present study, a selection of standard analytical methods described in section 2.9 was used, modified and combined, considering advantages and disadvantages of each method, to finally develop a complete protocol for studying tall oil solubility in black liquors. The experimental setup and preliminary tests are presented below, which culminated in the final analytical protocol (described in detail in section 0).

4.1   EXPERIMENTAL SETUP

The experimental work was conducted in small-scale using 15 or 50 mL plastic test tubes with 5 mL of synthetic black liquor. The small scale enabled many different tests to be done simultaneously, reduced the required volumes of chemicals, such as organic solvents, and minimized the generation of chemical wastes. Initially, only tall oil and inorganic salts were included in the synthetic samples (as shown in Tables 1 and 2), and the liquor was incubated at 90°C for 30 min to fully dissolve the tall oil components and form the soap. After centrifuging (4,000 rpm for 10 min), the tubes were transferred to -20°C to freeze for about 2 hours. Then the top frozen part (the non-soluble soap) was skimmed and subjected to washing, acidification (based on Sithole (1993), drying, and/or solvent extraction (based on Voss and Rapsomatiotis (1985))and the tall oil recovery was determined for each test gravimetrically or colorimetrically.

The preliminary tests done to develop the model system for the tall oil solubility studies are summarized in Table 5 , along with a brief description of experimental conditions. All tests were conducted in duplicate unless stated otherwise. The outcome in term of tall oil recovery for each test is presented and discussed in Section 4 of the Results and Discussion.

 For the colorimetric analysis of tall oil soap, the method described by Sithole (1993) was selected, which involved complexing the extracted tall oil fatty and resin acids with copper ions and extracting the complexes into hexane. These copper complexes color the solution blue, and the intensity of the color is relative to the concentration of the fatty and rosin acids, enabling their accurate estimation using a spectrophotometer (Baker, 1964). Based on the absorbance spectra of tall oil (see Figure 10 in section 0), the wavelength of 677 nm was selected for tall oil estimation due to peak absorbance. To correct for the baseline increase, the wavelength of 497 nm was chosen, and the respective absorbance was subtracted from the one at 677 nm for each subsequent sample analysis. Finally, method calibration curves using standard solutions of known amounts of tall oil fatty acids, rosin acids, and oleic acid (for comparison) was established.

Table 5. Summary of the preliminary tests using simplified synthetic liquors (inorganic salts plus tall oil). All tests were conducted in duplicate, except 3 and 4 (single trials).

Test #	Liquor part	Experimental description
1.	SS	Water washed by adding 40 mL of warm water, centrifuging (4,000 rpm for 10 min), freezing (2h at -20°C), skimming top frozen part in tarred tray, drying overnight at 90°C and weighing.
2.	SS	Dried overnight at 90°C and weighed.
3.	SS	Extracted with 10 mL acetone, solvent phase evaporated and weighed.
4.	SS	Extracted with 15 mL hexane, solvent phase evaporated, and weighed.
5.	SS	Skimmed soap was acidified with 1.5 mL of 6N HCl, extracted with 25 mL acetone, then solvent phase was evaporated, and tube weighed.
6.	SS	Skimmed soap was acidified with 1.5 mL of 6N HCl, extracted with 25 mL hexane, then solvent phase was evaporated, and tube weighed.
7.	SS	Extracted 5x with 15 mL MBTE, solvent phases combined, evaporated, and weighed. Residual soap in liquor (after skimming) extracted twice with 15 mL MTBE, solvent phases combined, evaporated, and weighed.
8.	SS	pH adjusted to 9 and extracted 5 times with 15 mL MTBE, then solvent phases combined and evaporated, and tarred tube weighed.
9.	SS	Diluted 4 times, extracted twice with 15 mL MTBE, then solvent phases combined and evaporated, and tarred tube weighed.
10.	SS	Diluted 4 times, pH adjusted to 9, and extracted twice times with 15 mL MTBE, then solvent phases combined, evaporated, and weighed.
11.	SS	Skimmed soap was dried overnight at 90°C and weighed. Residual soap in liquor (after skimming) was dried for about 48h at 90°C.
12.	WL	Dried overnight at 90°C, extracted twice with 8 mL MTBE, then solvent phases were combined and evaporated, and tarred tube weighed.
13.	SS and RL	Extracted 2x with 8 mL MTBE, then solvent phases combined, evaporated, air dried, and analyzed colorimetrically. Leftover from extraction was dried and analyzed colorimetrically. Residual soap in liquor (after skimming) was extracted 2x with 8 mL MTBE, solvent phases combined, evaporated, dried, and analyzed colorimetrically.
14.	WL	Dried overnight at 90°C, extracted with twice with 10 mL MTBE, then solvent phases combined, evaporated, and analyzed colorimetrically.
15.	SS	Dried overnight at 90°C, acidified with 0.375 mL 6N HCl, and analyzed colorimetrically. Residual soap in liquor (after skimming) was dried overnight at 90°C, acidified with 0.375 mL 6N HCl, and analyzed colorimetrically.
16.	WL	Dried overnight at 90°C and analyzed colorimetrically.
17.	WL	Dried overnight at 90°C, acidified with 0.375 mL 6N HCl, and analyzed colorimetrically.
18.	inorganic salts only	Black liquor with only inorganic salts (no oil) were dried overnight at 90°C and analyzed colorimetrically.
19.	WL	Effect of pH on solvent extraction: pH adjusted to 7, 9 and as-is (12.8), followed by 2 times extraction with 10 mL MTBE, solvent evaporation and colorimetric analysis.
20.	SS and WL	Effect of number of solvent extractions: 2, 3, and 4 times extraction of skimmed soap with 10 mL MTBE, solvent evaporation and colorimetric analysis. Whole liquor was extracted 2 times with 10 mL MTBE, solvent evaporated and analyzed colorimetrically.

SS, skimmed soap; WL, whole liquor; RL, residual liquor

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4.2 PRELIMINARY TESTS TO DEVELOP THE MODEL SYSTEM

4.2.1 Soap formation and skimming procedure

Initially, a process for preparing the synthetic black liquor (BL) and separating (skimming) the soap on was established using mixtures of the inorganic salts (see Table 2) and purified tall oil fatty acids. The mixtures were incubated at 90°C for 30 min for soap formation, as described in previous black liquor studies (Lenz, 1977). Lenz (1977) reported that the tall oil soap in black liquors separates very rapidly in laboratory conditions, even in as little as 3 min. However, we decided to incubate the synthetic black liquor for 30 min to make certain that the tall oil components were dissolved completely, and soap separation has finished.

Due to the small volumes involved in this lab-scale study, separating the tall oil soap from test tubes using traditional soap skimming methods (e.g. decanting or manual skimming) proved to be challenging and prone to reproducibility errors. Therefore, a modified process was developed that involved the freezing of the black liquor sample, after incubation, and transferring the frozen top part (tall oil soap plus a small part of the liquor) into a new tube.

4.2.2 Gravimetric analysis of skimmed soap

Next, attempts were made to establish a simple gravimetric method for the determination of the recovered tall oil soap. Gravimetric determination is a simple an inexpensive method but is not generally preferred in assaying liquors from industrial processes due to many interferences, which would have to be filtering or washed out (Backa, Brolin, & Nilvebrant, 1989). It was found that simply drying and weighing the recovered soap led to overestimation (135% tall oil recovery), probably due to Na salts carried over from BL (Test 2, Table 6).

Table 6. Tall oil recovery tests of skimmed soap by gravimetric analysis. Effect of washing, drying, and solvent (acetone, hexane, MTBE) extraction on tall oil recovery % (average ± standard error, where sample $n \geq 2$).

Test		Tall Oil Recovery %	Notes/concerns
1.	Skimmed soap after washing with water	31.0 ± 6.2	low soap recovery
2.	Dried skimmed soap (no wash)	135.4 ± 5.3	above 100% (overestimating)
3.	Acetone extraction	135.6	precipitation
4.	Hexane extraction	-	no phase separation; precipitation
5.	Acidified acetone extraction	7 ± 3.1	no phase separation; precipitation
6.	Acidified hexane extraction	148.2 ± 23.6	precipitation; high deviation
7.	MBTE extraction	60.0 ± 1.2	multiple extractions
	a. MTBE extraction of residual soap (in BL)	4.4 ± 1.2	low residual soap

On the other hand, washing the recovered soap part with water before drying and weighing resulted in low recovery, 31% (Test 1, Table 6). Although gravimetric determination could provide a comparative analysis of tall oil in the present solubility study, it was not chosen for the following experiments due to significant interferences from black liquor components, such as inorganic salts and lignin.

4.2.3   Solvent extraction and gravimetric estimation

Consequently, solvent extraction of the tall oil soap deemed necessary. Acetone and hexane had poor extraction performance with precipitations forming and had no phase separation that was visible (Tests 3 and 4, Table 6). Furthermore, adding acid to these solvents did not seem to improve the extraction (Tests 5 and 6, Table 6).

Two extraction methods commonly referenced in tall oil literature were one by Saltsman and Kuiken (1959), involving many steps of acidification and extraction of acetone-methanol-petroleum ether, and another by Voss and Rapsomatiotis (1985), who reported one-step extraction with methyl *t*-butyl ether (MTBE) with optimum in alkaline conditions (pH 9). MTBE-extraction was selected due to requiring fewer steps, using less toxic chemicals and its applicability to alkaline solutions such as in kraft pulping black liquors. The gravimetric analysis of skimmed and MTBE-extracted tall oil soap showed 60% recovery, while about 4% tall oil soap was extracted from the remaining BL solution (Test 7, Table 6).

Optimization of the solvent extraction was also attempted (multiple extractions, pH, sample dilution, and sample drying) to improve the overall extraction performance but led to overestimation ranging from 116 up to 230% tall oil recovery (Tests 8-12, Table 7), most probably due to sodium salts carried over from the black liquor.

Table 7. Tall oil recovery tests using solvent extraction (MTBE) followed by gravimetric analysis. Effect of pH change to 9, sample dilution and sample drying on tall oil recovery % (average ± standard error).

Test	Tall Oil Recovery %	Notes/concerns
8. Skimmed soap at pH 9	79.2 ± 2.8	5 extractions were needed; 1st extraction yield double than in test 7 (pH 12+)
9. Diluted skimmed soap, no pH change	115.7 ± 58.9	high deviation
10. Diluted skimmed soap at pH 9	116.0 ± 4.2	2 extractions; may need more
11. Dried skimmed soap	230.5 ± 3.0	above 100% (overestimating)
a. Dried leftover soap (dissolved in BL)	165.1 ± 88.3	above 100% (overestimating); very high deviation
12. Total soap (no skimming), no pH change (pH 12+)	120.0 ± 3.6	above 100% (overestimating)

4.2.4   Solvent extraction and colorimetric estimation

Based on the above results, we decided to employ a spectrophotometric method instead of a gravimetric one to estimate more accurately the recovered soap content. The method described by Sithole (1993) was applied, as described in sections 2.9.4, 4.1 and 0.

Since MTBE was used in the previous soap extraction, an experiment was conducted to investigate if hexane could be substituted with MTBE in the colorimetric analysis. This could eliminate the solvent evaporation step and reduce the number of the different chemical required. However, hexane showed a better response (higher absorbance) than MTBE, as shown in Figure 10, which means that

the copper-fatty acid complexes had greater solubility in hexane than MTBE. Therefore, choosing hexane as the solvent in colorimetric analysis should provide higher sensitivity, i.e. lower amounts of tall oil can be detected using this method. Hexane was ,in fact, the preferred solvent in the original colorimetric method by Sithole (1993).
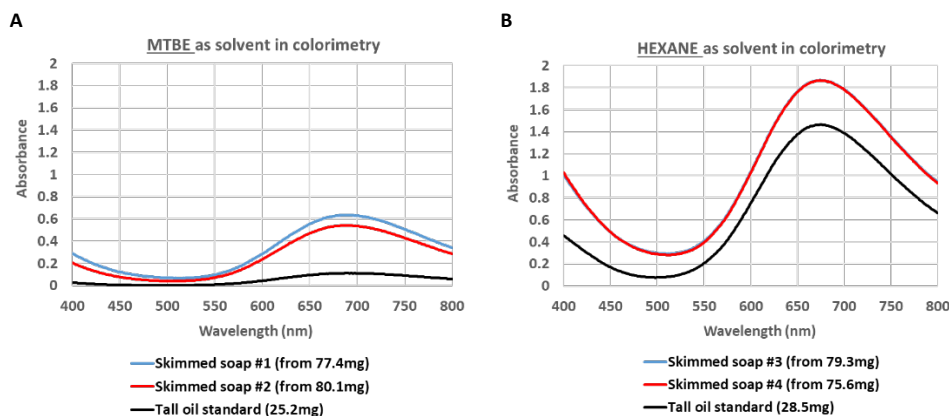

Figure 10. Light absorbance spectra of tall oil standard and skimmed soap to select the best organic solvent for optimum method response. A. MTBE; B. Hexane.

Applying the colorimetric method to oven-dried skimmed soap after MTBE extraction led to 21.1% estimated recovery, while very little tall oil was found in the leftover from extraction and in the residual black liquor (Test 13, Table 8). This could either mean poor solvent extraction or isomerization due to the heat of some of the rosin acids (e.g. levopimaric acid) that could inhibit the recovery of tall oil (Voss & Rapsomatiotis, 1985).

Table 8. Tall oil recovery tests using colorimetric analysis. Effect of sample drying, acidification and combinations with solvent extraction on tall oil recovery % (average ± standard error).

Test	Tall Oil Recovery %	Notes/concerns
13. Dried skimmed soap after MTBE extraction	21.1 ± 6.3	low recovery; visible peak
a. dried leftover from extraction	2.6 ± 0.6	very small peak
b. dried residual soap (dissolved in BL) MTBE-extracted	2.4 ± 0.5	no visible peak
14. Total soap in BL after MTBE extraction and drying	3.7 ± 0.3	no visible peak
15. Skimmed soap dried and acidified	2.1 ± 0.0	no visible peak
a. leftover from skimming	4.8 ± 1.7	high baseline; no visible peak
16. Total soap in BL after drying	9.5 ± 1.4	high baseline; no visible peak
17. Total soap in BL after drying and acidification	6.6 ± 1.2	high baseline; no visible peak
18. BL inorganic salts only	-	no visible peak; 0 absorbance
19. Effect of pH before extraction	2.5 - 76.6	max at pH 9
20. Effect of number of extractions	41.9 - 43.0	max at 2 extractions
a. total soap in BL	73.1 ± 1.1	after 2 extractions

The same pattern was also observed when the total black liquor sample (no skimming) was extracted with MTBE and dried (Test 14, Table 8), confirming the problem in this approach. Another reason for the low tall oil measurements could be the low response of the colorimetric method, which is very sensitive to pH (Lowry & Tinsley, 1976). Since residual alkali from the black liquor could significantly affect the pH, the effect of acidification of samples of MTBE-extracted tall oil soap was investigated. Again, this resulted in very low recovery, high baseline and no visible peak in the spectra analysis (Tests 15-17, Table 8). As a negative control, liquors with only inorganic salts (no tall oil) did not show any visible peak at 677 nm (Test 18, Table 8).

Therefore, in the subsequent tests, the solvent in the extracted soap was only air dried before performing the colorimetric analysis, and no acidification was performed. Furthermore, optimization of the solvent extraction was attempted to improve the method's performance in estimating the recovered tall oil. First, the effect of sample pH in the solvent extraction of total soap was studied (Test 19, Table 8). Recovery was very low in the unadjusted sample (pH 12.8), while at pH 9 was the highest and slightly dropped at pH 7 (Figure 11). Voss and Rapsomatiotis (1985) also reported the optimum pH for extracting tall oil from pulp mill effluents. Oven-drying the extracted soap had a minor effect on recovery, which means that the pH during extraction seems to be of greatest importance. Still, only three quarters of the total soap in the black liquor were extracted and were measurable. However, this methodology could be valid to study the solubility of tall oil by comparing the yields with the maximum measurable soap of 76.6%.
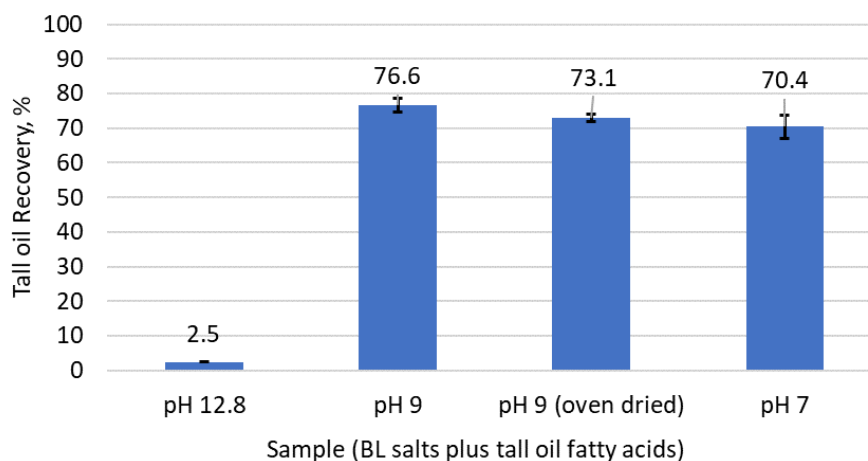

Figure 11. Effect of pH in MTBE extraction on estimating the total tall oil soap in the synthetic black liquor by colorimetric analysis.

Next, the number of extractions was studied to observe if more extraction steps were needed to improve the recovery and close the gap to 100% (Test 20, Table 8). Performing the above optimized method (MTBE extraction at pH 9 and colorimetry) on skimmed soap led to an estimated tall oil recovery of 41.9 to 43.0% with a small deviation between replicates, while 14.0-18.1% tall oil was found in the remaining (after skimming) liquor (Figure 12). The number of solvent extractions didn't seem to affect the estimation, so two extraction steps were

deemed sufficient. Applying the above method to the total (not skimmed) black liquor led to 73.1% recovery of tall oil (Figure 12), which was very similar to the previous results (Figure 11) and thus confirming the reproducibility of the method.

Figure 12. Tall oil recovery in defined black liquor samples before and after skimming using solvent extraction and colorimetric analysis.

4.2.5   Colorimetric analysis of different mixtures of tall oil fatty and rosin acids

The developed analytical methodology was tested on various mixtures of tall oil fatty acids (TOFA) and tall oil rosin acids (TOR). The response (mg of oil equivalents) of the colorimetric method on standard solutions of 100% TOFA and 100% TOR, and their mixtures (% by weight) 20-80, 40-60, 50-50 is presented in Figure 13. In solutions close to 100% TOR the method had a slightly higher response than when 100% TOFA were present.

However, the realistic range of TOFA-TOR compositions found in kraft pulping black liquors of softwoods is from 40-60% to 60-40%, or TOFA to TOR ratio of 0.7 to 1.3 (Lenz, 1977; Uloth et al., 2009), which is considered optimum for tall oil soap recovery (Lenz, 1977). In that range, the method was not affected and responded the same amount (mg) of total tall oil (Figure 13). Since the method was found applicable for different mixtures of TOFA and TOR, it was used in the following experiments studying the effect of fatty acid addition on improving tall oil recovery.
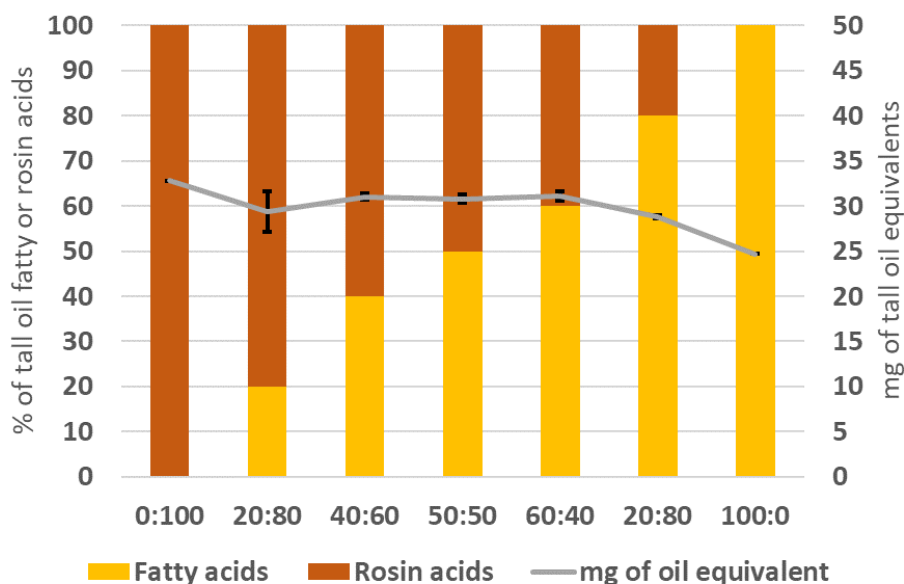
Figure 13. Colorimetric analysis of tall oil fatty acids, rosin acids, and their mixtures.

4.2.6 Optimizing soap skimming in mixtures of fatty and rosin acids

All previous soap skimming tests were done with only the fatty acids fraction of tall oil. When synthetic liquors were prepared with tall rosin acids and mixtures with fatty acids, differences in soap formation were observed, as the photo of the tubes in Figure 14 revealed. Most of the formed soap in 100% rosin acids sample (Figure 14.B) was precipitating at the bottom and not rising on top, compared to the 100% fatty acid sample (Figure 14.A) where most soap gathered on top. Their 50-50% mixture had soap accumulating on top, as well as throughout the tube (Figure 14.C).
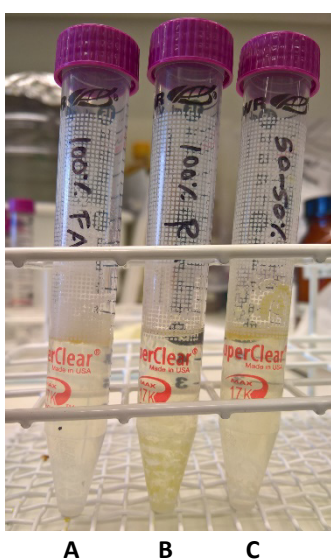

Figure 14. Photo of synthetic black liquor with inorganic salts (Table 2) and (A) 100% fatty acids, (B) 100% rosin acids, and (C) 50-50% mixture (by weight).

Therefore, attempts were made to optimize the soap skimming of mixtures of tall oil and fatty acids, concerning settling time and temperature before skimming. The rationale was to develop a process that leads to tall oil soap recovery high enough so that the solubility study can generate meaningful results, applicable to the tall oil recovery system of the kraft pulping mills.

Multiple test tubes with synthetic liquor that included inorganic salts and 50-50% mixtures of tall oil fatty and rosin acids. Incubation at 90°C for 30 min followed as before. Then, the samples were left to settle at; 1) -20°C for 2 h to freeze and then the top part skimmed; 2) -20°C for 30 min and then the liquor part decanted leaving behind the top soap pellet; 3) -20°C for 48 h to freeze completely, then stored at 4°C for 5 days before the liquor part decanted leaving behind the top soap pellet for further analysis. Tall oil recovery was estimated colorimetrically after solvent extraction as described in Materials and Methods (section 0).

1) Settling at -20°C for 2 h to freeze and then the top part skimmed

In the first test, the samples were left to freeze for 2 h and then the top part was skimmed into a new tube for tall oil recovery analysis. No soap pellet was visible in frozen tubes. Two control samples with the same composition (inorganic salts and a mixture of fatty and rosin acids) were prepared and analyzed directly to verify the analytical method. The tall oil recovery of the control tubes was 99% on average (Figure 15, samples 3-4), confirming the accuracy of the established experimental procedure (solvent extraction and colorimetry) in measuring the tall oil content in synthetic black liquors correctly. However, the tall oil estimated in the skimmed soap was low, 9-12%, while most remained soluble in the liquor (Figure 15, samples 1-2).
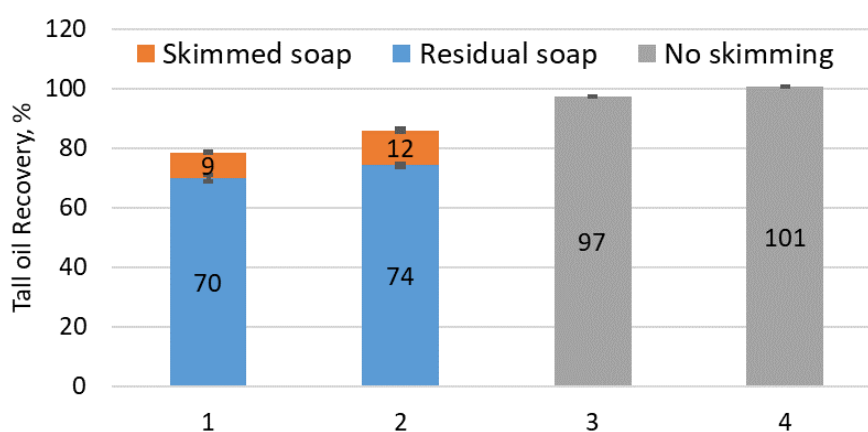

Figure 15. Tall oil recovery (%) in synthetic liquor samples (1-2) with 50-50% fatty and rosin acids, after settling at -20°C for 2 h and then skimmed. Control samples (3-4) included the same synthetic liquor components but analyzed without skimming. Error bars represent the standard deviation of the colorimetric measurements.

2) Settling at -20°C for 30 min and then the liquor part decanted leaving behind the top soap pellet

In this test, the samples stayed only 30 min at low temperature before skimming. There was a need to repeat centrifugation for the soap to form a pellet on top of the tube. Generally, less soap was observed to form on top than in samples 1-2 (skimmed frozen). However, the liquor could be carefully decanted to leave behind the formed soap in the tube facilitating further analysis. Tall oil recovery in the skimmed soap ranged from 17 to 21% (average 18%), while a significant residual amount of tall oil was estimated in the liquor (not skimmed), 66% on average (Figure 16).
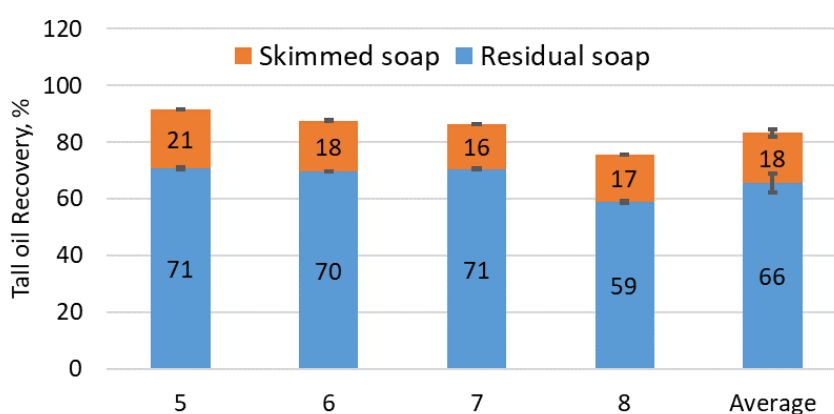

Figure 16. Tall oil recovery (%) in synthetic liquor samples (5-8) with 50-50% fatty and rosin acids, after settling at -20°C for 30 min and then the soap separated by decanting the liquor. The average recovery of 5-8 is shown in the last column. Error bars in 5-8 represent the standard deviation of the colorimetric measurements, while the standard error of 5-8 is shown as error bars in the average column.

3) Settling at -20°C for 48 h to freeze completely, then stored at 4°C for 5 days before liquor decantation to separate the soap

Next, some samples were left to settle for longer times at -20°C (48 h) and 4°C (5 days) than the previous samples, in order to evaluate the effect on soap skimming. The samples were centrifuged again after settling time passed for the soap to form a pellet on top to be separated by decanting the liquor off. Interestingly, the tall oil recovery of the skimmed soap was higher than the previous tests (samples 1-8), ranging from 47 up to 63% (55% on average, Figure 17, samples 9-12).
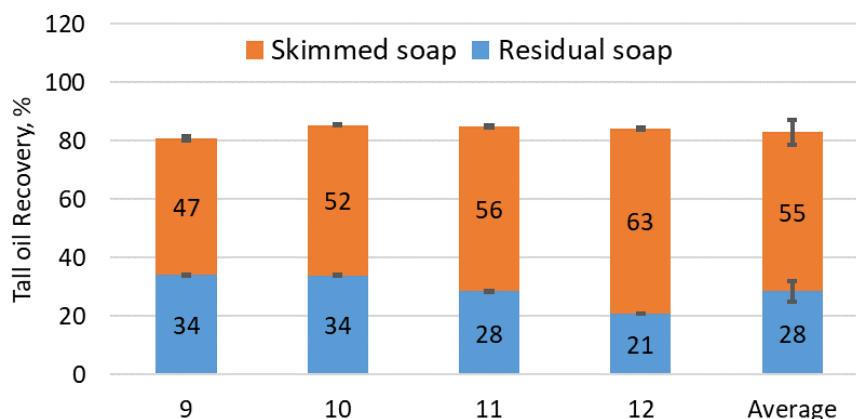
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Figure 17. Tall oil recovery (%) in synthetic liquor samples (9-12) with 50-50% fatty and rosin acids, after freezing at -20ºC for 48 h and settling at 4ºC for 5 days before by decanting the liquor to separate soap. The average recovery of 9-12 is shown in the last column. Error bars in 9-12 represent the standard deviation of the colorimetric measurements, while the standard error of 9-12 is shown as error bars in the average column.

As expected, the residual soap content of the synthetic liquor after skimming was significantly lower than the previous tests, confirming that more soap was insoluble and skimmed in samples 9-12 (Figure 17). A photo of the formed soap in these samples is shown in Figure 18.
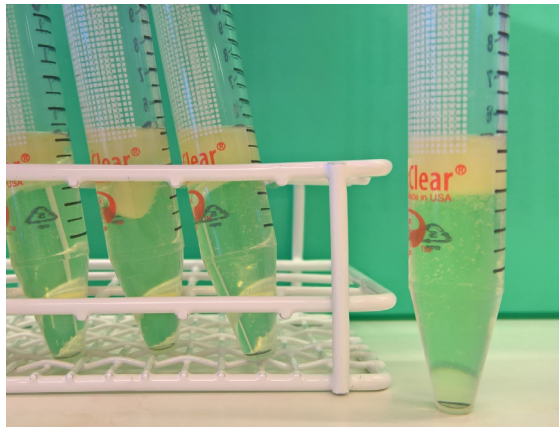

Figure 18. A photo of the formed soap accumulated on top of samples 9-12 from Figure 17. Some soluble soap can also be seen throughout the liquor.

Although the prolonged settling (7 days in total) at low temperatures resulted in more tall oil to be skimmed (samples 9-12), it was considered impractical for the solubility study. Therefore, additional qualitative tests were conducted to select a more practical protocol with shorter settling times that would yield adequate soap for the solubility studies. The test included preparation of synthetic liquors with different mixtures of fatty and rosin acids, incubation at 90°C for 30 min, as before, followed by settling at 90°C, or 4°C. Some samples were also kept at -20°C for a few hours, while some were only centrifuged after settling time passed. A summary of the qualitative results and description of conditions is presented in Table 9.

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Table 9. Summary of qualitative results on soap skimming potential of synthetic liquors with different mixtures of tall oil fatty acids (TOFA) and rosin acids (TOR) and settling times and temperatures.

			1	2	3	4
#	TOFA %	TOR %	centrifuge, 90°C overnight, centrifuge	centrifuge, -20°C for 4h, 4°C overnight, centrifuge	centrifuge, 4°C overnight, centrifuge	4°C overnight, centrifuge
A	100	0	fragile soap pellet, spreading while decanting	fragile soap pellet, not easy to separate by decanting liquor	compact soap pellet, easy to separate by decanting liquor	compact soap pellet, easy to separate by decanting liquor
B	75	25	n.p.	small soap pellet, able to separate by decanting liquor	compact soap pellet, easy to separate by decanting liquor	compact soap pellet, easy to separate by decanting liquor
C	50	50	n.p.	some soap on top, cannot separate by decanting liquor	small soap pellet, not easy to separate by decanting liquor	small soap pellet, not easy to separate by decanting liquor
D	25	75	n.p., pr.	n.p., pr.	n.p., pr.	n.p., pr.
E	0	100	n.p., pr.	n.p., pr.	n.p., pr.	n.p., pr.

n.p., no visible pellet

pr., precipitation

Incubating the samples at 90°C overnight did not seem to promote the soap separation, as there was almost no visible soap forming on top (Table 9, condition 1). On the other hand, storing the samples at low temperature (4°C) overnight led to the formation of an adequate amount of soap on the top (Table 9, conditions 2,3, and 4), but there were differences among the different mixtures. The samples with 100% fatty acids (A) formed more easily soap that collected on top. As the fatty acids content lowered, more soap was dispersed soap (soluble) throughout the tube, while at 75 and 100% rosin acids (D and E, respectively) the soap collected mostly at the bottom half of the test tube and precipitation was present. Overall, allowing the synthetic black liquor samples to settle at 4°C overnight provided a good amount of formed soap to study the soap skimming and tall oil solubility in the following experiments. Centrifuging before the settling did not seem to affect the soap formation, so it was omitted for time efficiency.

Finally, the effect of freezing the liquor on tall oil recovery was investigated. For that purpose, identical synthetic liquors that included inorganic salts and tall oil (50% fatty acids, 50% rosin acids) were prepared as described before and were either frozen (at -20°C), frozen and then heated (90°C for 30 min), or analyzed directly (control) for tall oil using the developed solvent extraction and colorimetric estimation. No significant effect on tall oil estimation was observed by freezing the liquors since almost all of the initial tall oil was recovered (Figure 19).

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Therefore, the freezing step was included in the tall oil solubility study methodology as it facilitated the soap skimming in such small working volumes (5 mL) in the test tubes.
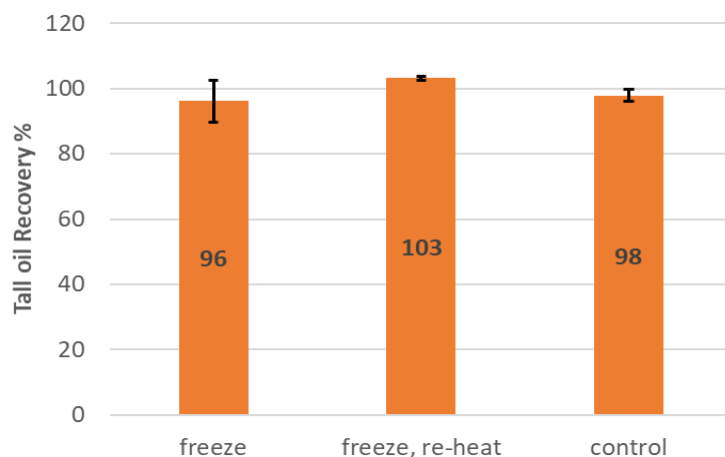

Figure 19. Effect of liquor freezing on tall oil recovery in synthetic liquors. Identical liquors with inorganic salts and tall oil (50% fatty acids, 50% rosin acids) were prepared, incubated (90°C for 30 min), settled (24h at 4°C), and frozen, frozen and incubated (90°C for 30 min), or analyzed directly (control) for tall oil using the developed solvent extraction and colorimetric estimation.

4.2.7 Test of the developed method in full synthetic liquors (tall oil, lignin, xylan, and organic acids)

Next, the developed method (tall oil extraction and colorimetric estimation) was tested in more complex synthetic liquors. Based on the defined compositions in Table 4, lignin, xylan, and/or organic acids were mixed with tall oil (50% fatty acids, 50% rosin acids) along with inorganic salts and these liquors were subjected to solvent extraction and tall oil estimation, as previously described. Furthermore, multiple extractions were performed to assess any effect of the increased organic load (e.g. lignin, xylan etc.) on extraction performance.

The analysis of the recovered tall oil showed that the addition of the other organic components commonly found in black liquors, especially the high lignin load, did not seem to interfere with the developed extraction and tall oil estimation. As shown in Figure 20, in total, 102% and 95% of initial tall oil were extracted from liquors with added lignin and full synthetic liquors, respectively. However, one additional extraction step deemed necessary to extract most of the tall oil in these more complex liquors. The 4th extraction was omitted for saving time and reducing chemicals use as very little tall oil was present in that final part. Therefore, for tall oil solubility experiments involving lignin three solvent extractions were performed.
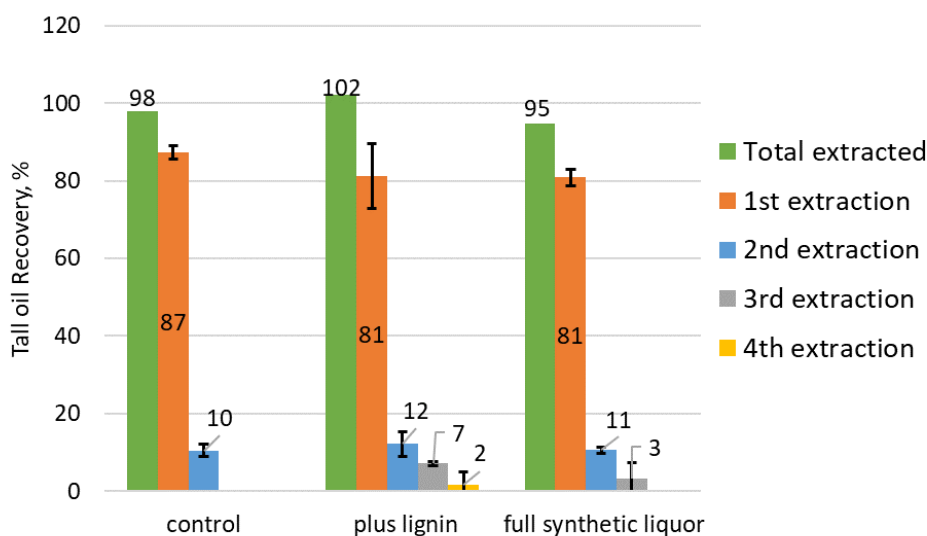
Figure 20. Effect of adding more organic components in the synthetic liquors on tall oil recovery and estimation. Synthetic liquors with inorganic salts and tall oil (50% fatty acids, 50% rosin acids) (control), plus lignin, and full synthetic liquor components (inorganic salts, tall oil, lignin, xylan, organic acids) were prepared, incubated (90°C for 30 min), settled (24h at 4°C), and analyzed for tall oil using the developed solvent extraction and colorimetric estimation.

4.2.8   Conclusion on method development

Based on the previous observations and optimization steps, a complete methodology for preparing synthetic black liquor samples and studying the tall oil solubility was developed. First, the synthetic liquor components are mixed and incubated at 90°C to form the tall oil soap. Next, the samples are frozen and skimmed, followed by organic solvent extraction and colorimetric analysis of the extracted tall oil to calculate the yield. A diagram of the main experimental steps is presented in Figure 21. The experimental details and conditions of each step are described in section 0 of the Materials and Methods.
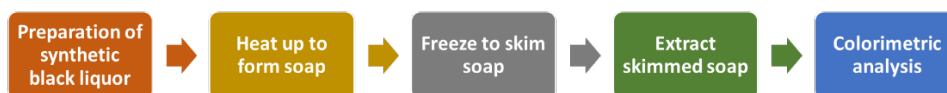

Figure 21. Main experimental steps of the developed model system to study tall oil solubility. Details are provided in section 0 of the Materials and Methods.

5 Results and Discussion

The experimental results of the tall oil solubility studies using the developed model system are presented and discussed in this section. The study starts with the effect of fatty acid to rosin acid content ratio, followed by the effect of lignin content on tall oil recovery in synthetic liquors and concluding with tall oil solubility experiments in real industrial black liquors.

5.1 EFFECT OF FATTY–ROSIN ACIDS RATIO ON TALL OIL RECOVERY USING SYNTHETIC LIQUORS WITH INORGANIC SALTS AND TALL OIL

The above experimental protocol (summarized in Figure 21) was applied to synthetic liquors with defined mixtures of tall oil fatty and rosin acids. Significant differences were observed in the tall oil soap solubility between the different mixtures.
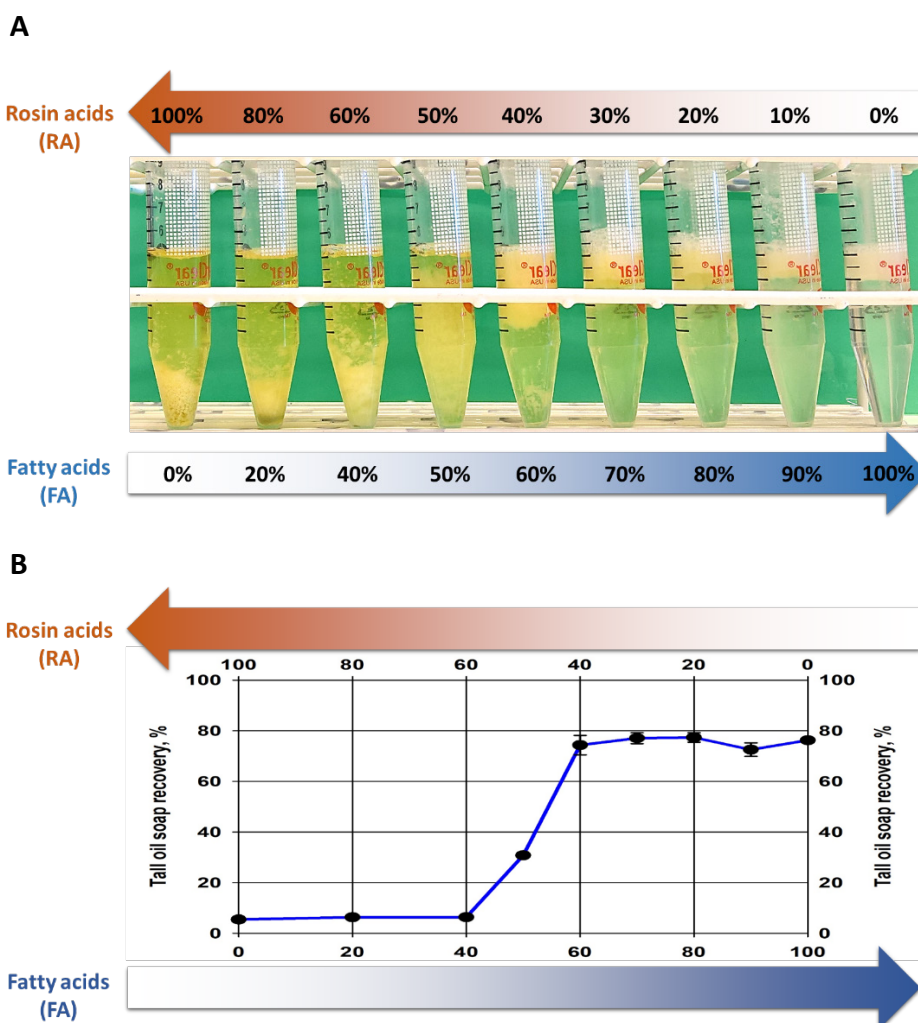

Figure 22. Solubility study of tall oil soap in the synthetic black liquors with mixtures of fatty and rosin acids at different ratios. A. photo of each sample. B. Estimated tall oil recovery of each skimmed soap from A. Error bars show the standard error of duplicates.

As shown in Figure 22.A, the samples with 100% and 80% rosin acids had very little soap accumulating on top, and most had precipitated or was in solution at the bottom half part. When the content of fatty acids in the mixture was 40% and above, less soap had precipitated and more had collected on top, facilitating its separation. Above 60% content of fatty acids, the soap precipitation started to disappear, and most of the tall oil soap had risen to the top of the tube. At the midpoint (50-50% fatty-rosin acids), the formed soap had dispersed throughout the liquor volume. The same pattern was also observed in the previous qualitative tests of fatty-rosin acid mixtures (Table 9), thus confirming the reproducibility of the developed protocol.

The skimming of the top part and quantitative analysis of tall oil soap verified the observed pattern of soap solubility. Tall oil recovery %, based on the tall oil content in the skimmed soap of each condition, is presented in Figure 22.B. Low recovery (5.4-6.3%) was estimated in samples with more than 60% rosin acids (below 0.7 TOFA-TOR ratios), while highest recovery was in samples with more than 60% fatty acids or a ratio of 1.5 (Figure 22.B and Table 10). The recovery progression pattern followed a sigmoid curve, with an inflection point (slowing down) around 50-50%, and a plateau above 60% fatty acids and 40% rosin acids.

Table 10. Tall oil recovery in the synthetic black liquors with mixtures of fatty and rosin acids at different ratios (each condition in duplicate).

#	TOR (% of oil)	TOFA (% of oil)	TOFA-TOR ratio	Tall oil recovery (% of initial tall oil)	Standard deviation
1	100	0	0.0	5.4	0.1
2	80	20	0.3	6.3	0.6
3	60	40	0.7	6.3	0.0
4	50	50	1.0	30.8	0.1
5	40	60	1.5	74.3	3.8
6	30	70	2.3	77.1	2.1
7	20	80	4.0	77.4	1.9
8	10	90	9.0	72.6	2.7
9	0	100	-	76.3	1.0

Tall oil soap recovery % (SR) could be efficiently described by a logistic model (Eq. 5), using the ratio (r) of fatty acids to rosin acids present in the synthetic liquor. Eq. 6 shows the resulting equation parameters that fitted well the experimental data (plotted in Figure 23).

$$SR(r) = 5.64 + \frac{69.86}{1+e^{-10.56\,(r-1.05)}}$$

Eq. 6

($R^2 = 0.998$; standard error of estimate 1.974; P < 0.0001)

Eq. 6 predicts that maximum soap recovery using the methodology in the present study is 5.64 + 69.86 = 75.50%, while lowest (when $r = 0$, i.e. no fatty acids present) is 5.64%. Furthermore, it shows that the inflection point of the curve is at $r = 1.05$, which means that the increase of the soap yield by adding fatty acids is becoming slower until it almost stops after r becomes 1.5-2.0.
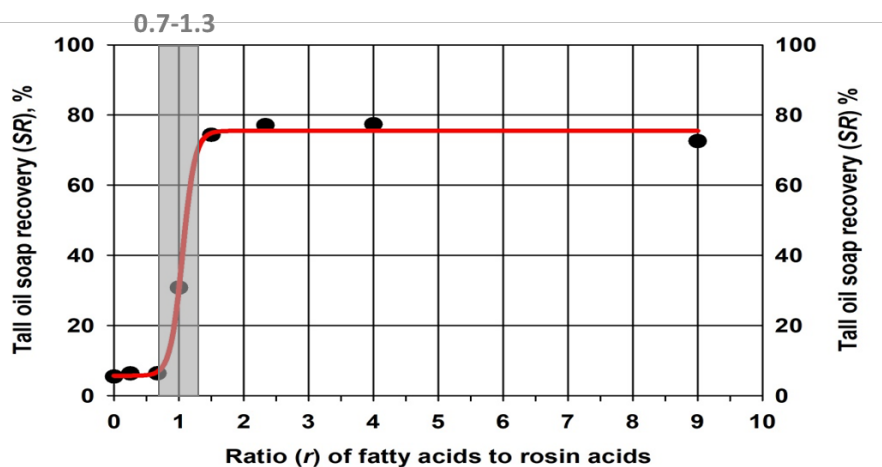
Figure 23. Effect of tall oil fatty acids to rosin acids ratio (*r*) in tall oil soap recovery (*SR*) using the methodology developed in the present study. The sigmoid regression equation (Eq. 6) is plotted in red. The grey area represents the typical range of fatty acids-rosin acids composition in industrial black liquors.

The TOFA-TOR ratios found in kraft pulping black liquors of softwoods typically range from 0.7 to 1.3 (Lenz, 1977; Uloth et al., 2009), as shown with grey in Figure 23. According to the predicted tall oil recoveries shown in Table 11 and depending on the "*r*" of the black liquor, there is still room for improvement by adding more fatty acids.

Table 11. Predicted tall oil recovery (SR) % in black liquors with different fatty acids to rosin acids ratios (r) using the Eq. 6.

r	*SR* (%)
0.70	7.3
0.80	10.3
0.90	17.5
1.00	31.6
1.10	49.6
1.20	63.6
1.30	70.8
1.40	73.8
1.50	74.9
1.60	75.3
1.70	75.4
1.80	75.5
1.90	75.5
2.00	75.5

For example, if the starting ratio is 1.2, then an increase to 1.5 (about 5% more fatty acids) could potentially lead to an 11% increase in tall oil yield. A study by Uloth et al. (2009) also reported that in lab tests the addition of tall oil fatty acids, or waste vegetable oils, could decrease tall oil soap solubility and therefore increase soap

skimming efficiency. An increase of fatty acid/resin acid ratio from 0.7 to 1.23 led to an increase of tall oil soap skimming efficiency from 50.2% to 71.8% based on total soap available (Uloth et al., 2009).

Thus, it appears as the addition of "extra" fatty acids can increase the yield of tall oil obtained, but how should that be done in the most economically favourable way? One strategy is of course to obtain some cheap quality of triglycerides and hydrolyse them to produce fatty acids – such qualities could be consumed cooking oil from restaurants. Another interesting possibility is to obtain the fatty acids from companies processing the recovered tall oil. In the latter case, some fatty acids should "circulate" and thereby increase the tall oil production. The latter strategy may have the advantage that of maintaining the control of the fatty acid composition.

Although these results are encouraging in terms of potential to improve tall oil yields by addition of fatty acids, they support the need to study the tall oil solubility in complete synthetic liquors (including lignin, carboxylic acids, and polysaccharides fractions, as shown in Table 4), as well as in real industrial black liquors to confirm the potentially beneficial effects of fatty acid addition on the efficiency of soap skimming.

5.2   EFFECT OF LIGNIN ON TALL OIL RECOVERY USING SYNTHETIC LIQUORS WITH INORGANIC SALTS, TALL OIL AND LIGNIN

Next, the experimental protocol was applied to synthetic liquors with defined mixtures of tall oil fatty acids, rosin acids and lignin to assess the effect of lignin on tall oil solubility. First, the effect of fatty acid to rosin ratio in the presence of a fixed amount of lignin (according to Table 4) was investigated (section 5.2.1). Then, the content of lignin varied and its effect on tall oil recovery was studied (section 5.2.2).

5.2.1   Effect of fatty acid-rosin ratio on tall oil recovery

Significant differences were observed in tall oil solubility between the different fatty acid-rosin mixtures in the presence of lignin. Addition of lignin in the synthetic liquor led to a decrease in tall oil recovery in the case of liquors with more than 50% fatty acids (ratio ≥ 1) (Table 12, Figure 24), similarly to what was previously observed in the absence of lignin (Figure 22). On the contrary, in synthetic liquors with more than 50% rosin (ratio < 1), the addition of lignin improved the tall oil recovery. The effect of fatty acid-rosin ratio followed the same trend as without lignin, i.e. addition of fatty acids improved tall oil recovery up to a plateau (around 60% fatty acids).
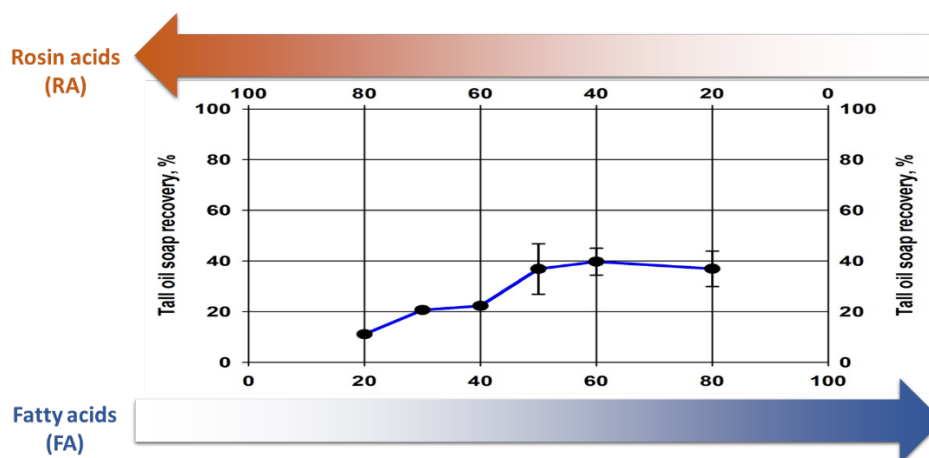
Figure 24. Solubility study of tall oil soap in the synthetic black liquors with mixtures of fatty and rosin acids in the presence of lignin. Error bars show the standard error of duplicates.

Table 12. Tall oil recovery in the synthetic black liquors with mixtures of fatty and rosin acids at different ratios when lignin was present as defined in Table 4 (each condition in duplicate).

#	TOR (% of oil)	TOFA (% of oil)	TOFA-TOR ratio	Tall oil recovery (% of initial tall oil)	Standard deviation
1	80	20	0.3	11.1	0.4
2	70	30	0.7	20.6	1.1
3	60	40	1.0	22.3	0.4
4	50	50	1.5	36.8	14.1
5	40	60	2.3	39.7	7.5
6	20	80	4.0	36.9	9.9

Tall oil soap recovery % (SR) in the case of lignin addition could be described by a logistic model (Eq. 5), based on the ratio (r) of fatty acids to rosin acids in the synthetic liquor. Eq. 7 shows the equation parameters that fitted the experimental data (plotted in Figure 25).

$$SR(r) = 9.68 + \frac{29.13}{1+e^{-3.58\,(r-0.97)}}$$

Eq. 7

($R^2 = 0.96$; standard error of estimate 3.57; $P < 0.05$)

Eq. 7 predicts that maximum soap recovery in the presence of lignin using the specific methodology in this study is 9.68 + 29.13 = 38.81%, while lowest (when r = 0, i.e. no fatty acids present) is 9.68%. Although the predicted high yield is about half than in the experiments without lignin, the lowest yield is about double when lignin is present and tall oil contains 100% rosin. In other words, on the one hand, lignin seemed to increase the solubility of tall oil fatty acids and thus reduced soap separation, on the other hand, decreased the solubility of the rosin part and therefore helped its separation. Furthermore, Eq. 7 shows that the inflection point of the curve (after which the increase of the soap yield by adding fatty acids slows down) is at r = 0.97 and the tall oil yield increase almost stops after r becomes 2 x 0.97 = 1.94, which are very similar to the predictions when lignin was absent (Eq. 6).

Note that the reported yields are based on our study method and do not necessarily translate to actual yields in pulp mills where conditions may differ. The trends and relative results, however, could apply to the industrial processes.
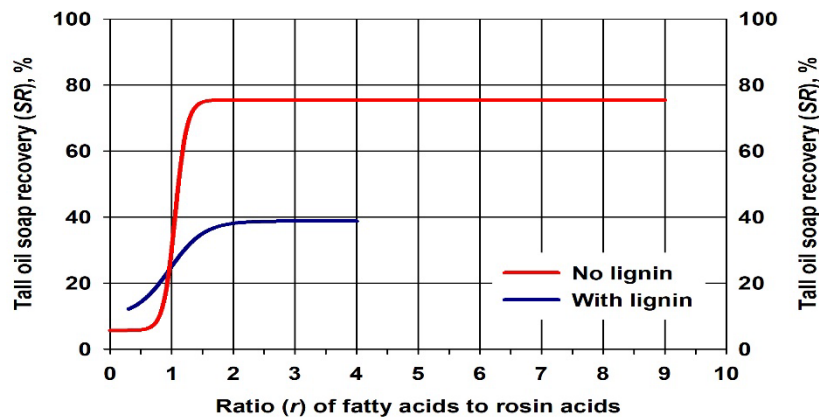

Figure 25. Effect of fatty acid-rosin acid ratio on tall oil recovery in the absence and presence of lignin (based on the amount of lignin typically expected in industrial black liquors, see Table 4).

5.2.2   Effect of lignin content on tall oil recovery

As more lignin was added to the synthetic liquor, tall oil recovery had a decreasing trend (Figure 26), which could be potentially attributed to either the increased viscosity and/or hydrophobicity of the black liquor that inhibit the formation and rising of tall oil micelles (soap) to the top. On the other hand, lowering the lignin content up to 50% improved tall oil recovery (Figure 26) and then dropped again. Therefore, it seems some lignin is beneficial to separate the tall oil (reduces its solubility), but too much can inhibit the recovery. This effect is not considered impossible in any way since lignin could have surface-active properties.
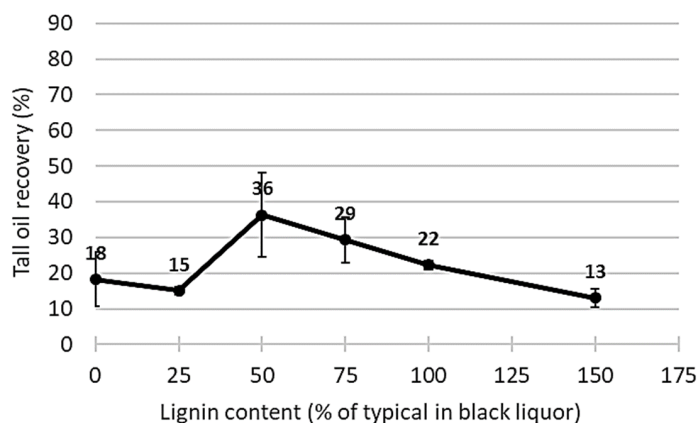
Figure 26. Effect of lignin content on tall oil recovery (at a fatty acids-rosin ratio equal to 1). The 100% lignin content is the typically expected amount of lignin in industrial black liquors (based on Table 4). Error bars show the standard error of duplicates.

However, the high deviation between some of the duplicate samples (especially at the peak) and the lab scale and conditions of the experiment make it difficult to quantify the exact increase in the oil yield that a pulp mill could achieve.

Nevertheless, these observations revealed another possible way to improve tall oil yield that is by reducing the amount of lignin present before the black liquor is concentrated and skimmed, which should be practically possible.

5.3   STUDY OF TALL OIL SOLUBILITY IN INDUSTRIAL BLACK LIQUORS

Our lab received samples of real industrial black liquors from Södra and SCA Obbola kraft pulp mills. We tested the developed skimming procedure and analytical method in the 'intermediate' dry matter liquors from both mills, 'Södra' (18.9% dry matter) and 'Obbola' (21% dry matter), as well as the effect of adding a small amount of fatty acids or rosin acids on tall oil yield.

More specifically, purified tall oil fatty acids or rosin acids were added in the industrial liquors to a final concentration of 1 g/L to each type. Industrial black liquors samples without any supplementation served as controls. After mixing and incubating all samples (at 90°C for 30 min), foam formed at the surface of the liquors indicating the formation and accumulation of micelles, most probably including tall oil (Figure 27).
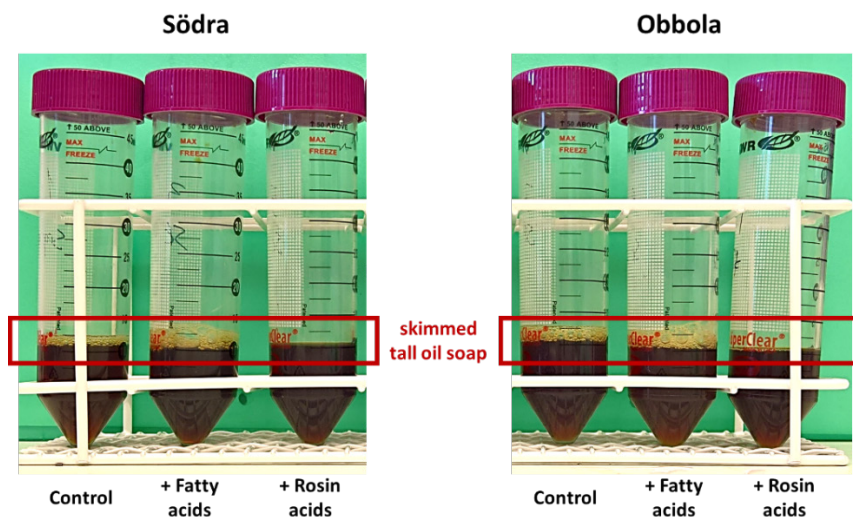

Figure 27. Photo of test tubes with original industrial black liquors from Södra and Obbola kraft pulp mills (controls) and supplemented with fatty acids or rosin acids (1 g per liter of black liquor) after incubation at 90°C for 30 min.

The amount of foam in the samples with added fatty acids seemed more than in the control sample, while in the samples with added rosin acids very little to no foam was observed. An attempt to quantify the tall oil from the top part of the liquors were followed to more accurately assess the effect of the additions on the tall oil yield.

Following settling and freezing, all samples (control and supplemented) were subjected to the same skimming protocol as described previously (section 0), and the extracted material was collected for analysis of tall oil content. The recovered material in all samples after solvent evaporation seemed to contain a small amount of oil along with a dark brown residue. However, when subjected to the analytical method (copper ions binding to tall oil fatty/rosin acids to form blue color) a zero

absorbance was measured and the blue coloring reagent turned green-brown. This could mean that some compounds in the extractables from the real industrial liquors were interfering with the photometric method. This phenomenon had not been observed in the synthetic black liquors.

After further trial and error (results not shown), the analytical method was modified to acidify the extracted material in an effort to (a) precipitate any extracted lignin molecules and (b) free up any metal salts of tall oil fatty and rosin acids to be able to bind with the copper ions, as suggested by Sithole (1993). Then, a second solvent extraction (hexane) was performed to further purify the extracted tall oil, followed by addition of the blue color (copper acetate) reagent and photometric analysis, as described in the Materials and Methods section.

Table 13. Analysis of industrial black liquors used in the present study and effect of fatty acid or rosin acid addition on tall oil recovery on these liquors.

Black liquor	Svartlut Södra	Blandlut Obbola
Solids content (%, w/v)	18.9	21
Fatty acids (mg/kg)	340	2640
Rosin acids (mg/kg)	390	1460
Fatty acids - Rosin ratio (r)	0.87	1.81
Total tall oil (sum of fatty and rosin acids, mg/kg)	730	4100
Density (kg/L)	1.11	1.10
Total tall oil in liquor (sum of fatty and rosin acids, g/L)	0.66	3.73

	Black liquor supplementation					
	Control	+ Rosin acids	+ Fatty acids	Control	+ Rosin acids	+ Fatty acids
Added fatty acids (g/L)	-	-	1	-	-	1
Added rosin acids (g/L)	-	1	-	-	1	-
Total fatty acids (g/L)	0.31	0.31	1.31	2.40	2.40	3.40
Total rosin acids (g/L)	0.35	1.35	0.35	1.33	2.33	1.33
Total tall oil in liquor (sum of fatty and rosin acids, g/L)	0.66	1.66	1.66	3.73	4.73	4.73
Fatty acids to rosin ratio (r)	0.87	0.23	3.72	1.81	1.03	2.56

	Settling and skimming using the developed protocol					
Tall oil in <u>skimmed soap</u> (fatty acid equivalents, in g per L of initial black liquor)	0.55 ± 0.08	0.66 ± 0.05	1.05 ± 0.02	0.52 ± 0.03	0.74 ± 0.10	1.51 ± 0.02

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Black liquor	Svartlut Södra			Blandlut Obbola		
Tall oil yield increase (%, based on control yield)	-	20	90	-	41	188
Overall tall oil yield (%, based on initial tall oil content)	84	40	63	14	16	32

By including the acidification step, a measurable amount of tall oil could be detected in the skimmed soap of the industrial liquors. However, the actual tall oil amount could be underestimated as the interfering compounds may not have been completely de-activated or removed. Table 13 summarizes the data from the tall oil recovery experiments from the two industrial black liquor samples, along with the analysis of the original black liquors by an external lab.

Since the actual amounts of tall oil may be underestimated due to method interferences, only relative conclusions can be made. Similar tall oil levels was measured in the skimmed soap of the control samples (no external fatty or rosin acids) from the Södra and Obbola liquors. Adding 1 g/L tall oil fatty acids (10% of total tall oil typically reported in black liquors) into the Obbola liquor almost tripled the tall oil yield, while 90% increase was observed in the Södra liquor. On the other hand, the addition of 1 g/L rosin acids led to a much smaller increase in tall oil yield in both liquors, about 20-41% (Table 13).

The above results align well with the previous observations from the synthetic black liquors (section 5.1, Figure 22), where more fatty acids greatly improved soap separation (reduced the oil solubility) while more rosin acids reduced tall oil recovery. Therefore, the potentially beneficial effects of adding externally fatty acids before soap skimming to improve tall oil yield were confirmed in real industrial black liquors. However, it is difficult to project the actual improvement at the mill based on the present study due to the small-scale experimental limitations.

6   Conclusions

The purpose of the project was to investigate if different types of chemical additions could improve the tall oil separation yield from black liquor (consumed pulping liquor from kraft pulping of wood). In order to investigate this in a controlled way, a small-scale simulation was developed based on a "synthetic" black liquor, which includes inorganic cooking chemicals, lignin, hemicellulose, sugar decomposition products, and tall oil fatty and rosin acids.

- A complete methodology for skimming and determination of recovered tall oil has been developed on synthetic black liquors based on solvent extraction and colorimetric analysis with good reproducibility. This method allows investigations of different parameters in small scale with high control over different conditions.

- The proposed methodology was found applicable on mixtures of tall oil fatty acids, rosin acids and lignin and was used to study the effect of fatty acid addition and the effect of lignin content on improving oil recovery.

- The presence of rosin acids significantly reduced soap separation, while increasing the fatty acid content up to 60-70% greatly improved soap recovery, opening up for a possibility to increase the content of fatty acids in the black liquor for increased separation.

- Addition of lignin in synthetic liquor with varying fatty acid and rosin acid ratios followed a similar trend. It decreased tall oil recovery in the case of liquors with more than 50% fatty acids (ratio ≥ 1) but slightly increased recovery in liquors with more than 50% rosin acids (ratio < 1). Furthermore, it seems some lignin promotes separation of the tall oil (reduces its solubility), while too much can inhibit its recovery.

- Studying tall oil solubility in real industrial liquors was more difficult than in synthetic mixtures, as some unknown compounds were interfering with the analytical method. However, after method modification, adequate amounts of tall oil could be measured in skimmed soaps from the real liquors and ones supplemented with either fatty acids or rosin. Adding fatty acids improved soap separation (reduced the oil solubility) while adding rosin acids had a much lower effect.

- The potentially beneficial effects of adding externally fatty acids before the soap skimming step to improve tall oil yield were confirmed in real industrial black liquors, but larger-scale experiments are recommended to better quantify the actual yield improvement at the mill.

7 Future projects

The goal of the present project was to find and test ways to improve tall oil yield in kraft pulp mills by studying the tall oil solubility in black liquors. The main focus has been on developing a small-scale system for simulating tall oil separation. The project has reached many challenges, but now a working method is established, although it is somewhat more laborious than we hoped for.

In concrete results, we have shown that the ratio between fatty acids and rosin acids is an important factor for the yield in tall oil separation, meaning that higher fatty acid content lead to an increased yield. The limitation with the studies so far is that the system used is a simplified "synthetic black liquor", where we have simulated the tall oil, lignin and the inorganic content of a kraft pulping black liquor at concentrations typical at tall oil separation, but we have not investigated the influence of other components, ionic strength, or reaction kinetics. Moreover, a large-scale trial is deemed necessary to assess the actual potential of yield improvements in an industrial setting and to perform a techno-economic analysis.

7.1 SUGGESTED SMALL SCALE EXPERIMENTS

1. Effect of other components present in industrial black liquors

Study the effect of sterols, carboxylic acids, polysaccharides, turpentines, and metals on tall oil separation by mixing them into the synthetic liquor and estimating the tall oil yield using the developed methodology.

2. Effect of ionic strength

We have some preliminary observations that ionic strength influences tall oil yield and this effect has also been reported in the literature using simple mixtures of fatty and rosin acids (Björklund Jansson & Nilvebrant, 2009). However, to increase ionic strength in black liquor without affecting the chemical recovery system and sodium sulphur balance is an intricate matter.

3. Effect of reaction kinetics

It has been previously suggested that soap separation is influenced by temperature (Foran, 1992); therefore the kinetics of the tall oil soap formation and separation (temperature, settling time) could be studied to model the system and suggest optimizations using the methodology reported in the present study.

7.2 LARGER SCALE TRIALS

A continuation of this project should also be focused on larger scale trials, preferably in a pulp mill industrial environment, to perform experiments and to gather data to accurately estimate the tall oil yield increase suggested by the small-scale experiments. These results enable a techno-economic analysis to assess the feasibility and profitability of manipulating black liquor in kraft pulping to increase tall oil recovery.

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TALL OIL SOLUBILITY IN INDUSTRIAL LIQUORS

Tall oil is one of the most valuable by-products from the kraft pulping of softwood. It has a broad spectrum of applications including chemicals, detergents and fuel to combustion engines, and is partly a renewable alternative to petroleum. Even if it is just a minor part of the wood that is converted to tall oil, the volumes produced are significant due to the massive amounts of kraft pulp that is produced. The value per ton of tall oil is also relatively high. High yield of the tall oil is thus important both for economic and environmental reasons.

In this study methods for increasing the yield of tall oil production has been developed. Specifically, this project investigates if the tall oil separation yield from black liquor (consumed pulping liquor from kraft pulping of wood) could be improved by different types of chemical additions, such as fatty acids.

It has been shown experimentally that the ratio between fatty acids and rosin acids is an important factor for the yield in tall oil separation, meaning that higher fatty acid content leads to an increased tall oil yield.

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