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LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

Faculty of Technology

Degree Program of Energy Technology

Bachelor's thesis

ALTERNATIVE LIQUID BIOFUELS FOR LIME KILNS

Meesauunin vaihtoehtoiset nestemäiset biopolttoaineet

Examiner: Prof. (Tech) Esa Vakkilainen

Supervisor: M.Sc. (Tech) Riikka Silmu

Lappeenranta 26.4.2012

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ABSTRACT

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Alternative liquid biofuels for lime kilns

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2012

38 pages, 12 figures, 5 tables, 2 annexes

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Keywords: lime kiln, liquid biofuel, kraft process, carbon dioxide emission, carbon tax

Causticizing plant is an important part of kraft pulp mill. It uses green liquor from recovery boiler as a raw material and consumes lime to produce white liquor, which is an important chemical used in pulping. Lime kiln is a part of the causticizing process. It is used to convert lime mud, a by-product obtained from the causticizing back to lime in high temperatures. This conversion requires a lot of energy.

The most common fuels used as energy source for lime kiln are heavy fuel oil and natural gas. In a modern pulp mill lime kiln is the only user of significant amount of fossil fuels. Replacing fossil fuels with biofuels can have prominent economical and environmental benefits. Interest in using biofuels as energy source of lime kiln has become a worldwide issue in the recent years. However fuels used for lime kiln have a lot of certain requirements.

The purpose of this work is to study the required characteristics from liquid fuels used in pulp mill lime kiln and to map suitable liquid biofuels already available in the markets. Also taxation of liquid biofuels compared to heavy fuel oil in Finland, Sweden and Germany is shortly introduced.

TIIVISTELMÄ

Lappeenrannan Teknillinen Yliopisto
Teknillinen tiedekunta
Energiatekniikan koulutusohjelma

Ossi Ikonen

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Kandidaatintyö

2012

38 sivua, 12 kuvaa, 5 taulukkoa, 2 liitettä

Tarkastaja: Professori Esa Vakkilainen
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Hakusanat: meesauuni, nestemäinen biopolttoaine, sulfaattimenetelmä, hiilidioksidipäästö, hiilidioksidivero

Keywords: lime kiln, liquid biofuel, kraft process, carbon dioxide emission, carbon tax

Kaustisointilaitos on tärkeä osa sulfaattisellutehdasta. Se käyttää raaka-aineenaan soodakattilalta saatavaa viherlipeää ja kuluttaa kalkkia tuottaakseen valkolipeää, joka on tärkeä keittokemikaali sellunkeitossa. Meesauuni on osa kaustisointilaitosta. Meesauunissa kaustisoinnista sivutuotteena saatava meesa muutetaan korkeassa lämpötilassa takaisin kalkiksi. Meesan muuntaminen kalkiksi vaatii paljon energiaa.

Meesauunin energianlähteenä käytetään yleensä raskasta polttoöljyä tai maakaasua. Modernissa sellutehtaassa meesauuni on ainoa merkittävä fossiilisten polttoaineiden käyttäjä. Fossiilisten polttoaineiden korvaaminen biopolttoaineilla voi antaa merkittäviä taloudellisia ja ympäristöllisiä hyötyjä. Biopolttoaineiden käytöstä meesauunin energianlähteenä on tullut viime vuosina maailmanlaajuisesti kiinnostava aihe. Meesauunin polttoaineilla on kuitenkin paljon tiettyjä vaatimuksia.

Tämän työn tarkoituksena on selvittää nestemäisiltä polttoaineilta vaadittavat ominaisuudet meesauunikäytössä, ja kartoittaa jo markkinoilla olevat sekä potentiaalisimmat käyttöön soveltuvat nestemäiset biopolttoaineet. Myös nestemäisten biopolttoaineiden energiaverotus verrattuna raskaaseen polttoöljyyn Suomessa, Ruotsissa ja Saksassa on esitelty lyhyesti.

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NOMENCLATURE

Abbreviations

1G	first generation
Al	aluminum
AFT	adiabatic flame temperature
C	carbon
CaCO ₃	calcium carbonate
CaO	calcium oxide
Ca(OH) ₂	calcium hydroxide
CFB	circulating fluidized bed
CO ₂	carbon dioxide
CPO	crude palm oil
CST	crude sulfate turpentine
CTO	crude tall oil
DTO	distilled tall oil
EU	european union
EU ETS	european union emissions trading scheme
Fe	iron
GHG	greenhouse gas
GJ	gigajoule
H ₂ S	hydrogen sulfide
ITP	integrated thermal process

LHV	lower heating value
LMD	lime mud dryer
Mg	magnesium
N	nitrogen
Na	sodium
NaOH	sodium hydroxide
NO _x	nitrogen oxides
NPE	non-process element
Na ₂ CO ₃	sodium carbonate
rpm	rounds per minute
P	phosphorus
PAO	palm acid oil
S	sulfur
Si	silicon
SO ₂	sulfur dioxide
TRS	total reduced sulfur

1 INTRODUCTION

Worldwide political attention to reduce fossil fuel carbon dioxide emissions has increased significantly in recent years. Existing environmental agreements, like international Kyoto Protocol, which came into force in 2005 and The EU Energy Tax Directive 2003/96/EC are made to control the industrial use of fuels in different countries.

With rising energy costs and new environmental regulations in the past years, many kraft pulp mills have made it a priority to reduce their energy consumption and operation expenses. Lime reburning kiln is the biggest user of fossil fuels and only part of the mill, which needs significant purchasing of fuel. Fluctuating prices for fossil fuels and more stringent carbon taxes has made lime kiln energy consumption an important issue impacting the overall pulp mill profitability.

Lime kiln operating expenses can be decreased with increasing the thermal efficiency of the kiln and using new fuels for the combustion process. Most of lime kilns use heavy fuel oil or natural gas as their energy source, but many mills have interest to replace them with alternative renewable fuels in the future. Operation of the lime kiln affects to the whole pulp mill and must stay stable to produce acceptable quality lime and to keep pulp products from the mill good-quality.

Many things have to be considered when replacing the traditional fuels used in the kiln. Availability, heating value, chemical composition and combustion behavior of the alternative fuels are important matters when examining the effects of replacing on combustion, flue gas emissions and economy of the pulp mill.

Aim of this study is to examine the requirements of lime kiln fuel and to find the best fuel substitutes already available. This study is focused only on liquid biofuels, as liquid fuels are easier to transport and handle and have more similar combustion behavior compared to traditional fuel oil than solid fuels. For this study is chosen the most potential liquid biofuels for the future use, some of which are already in use in few kilns. Also taxation regulations of liquid biofuels compared to heavy fuel oil in industrial heat production in Finland, Sweden and Germany is shortly introduced.

2 RECAUSTICIZING PROCESS IN KRAFT PULP MILL

Efficient and closed chemical recovery is great benefit of the kraft pulp mill process. It makes recirculation of cooking chemicals in the process possible while using only little amount of makeup chemicals. Reausticizing plant is important part of chemical recovery at pulp mill. It uses green liquor from recovery boiler as raw material and consumes lime, calcium oxide (CaO) to produce white liquor, which is an important chemical used in pulping. (Järvensivu et al. 2001, 630)

The reausticizing process has two targets, to produce clean, hot white liquor containing minimum amount of unreactive chemicals for the cooking process, and prepare clean and dry lime mud to burn in the lime kiln for reuse as lime with minimum energy usage. (Gullichsen & Fogelholm 1999, 135)

Two important reactions of reausticizing are slaking and causticizing. When green liquor is mixed with lime (CaO) it slakes with water and forms calcium hydroxide (Ca(OH)_2). Calcium hydroxide continues to react with sodium carbonate (Na_2CO_3) in green liquor forming sodium hydroxide (NaOH), main compound in white liquor and also calcium carbonate (CaCO_3), called lime mud as by-product. (Gullichsen & Fogelholm 1999, 139)

Figure 1 shows causticizing process as a part of the kraft pulp mill chemical recovery circuit.

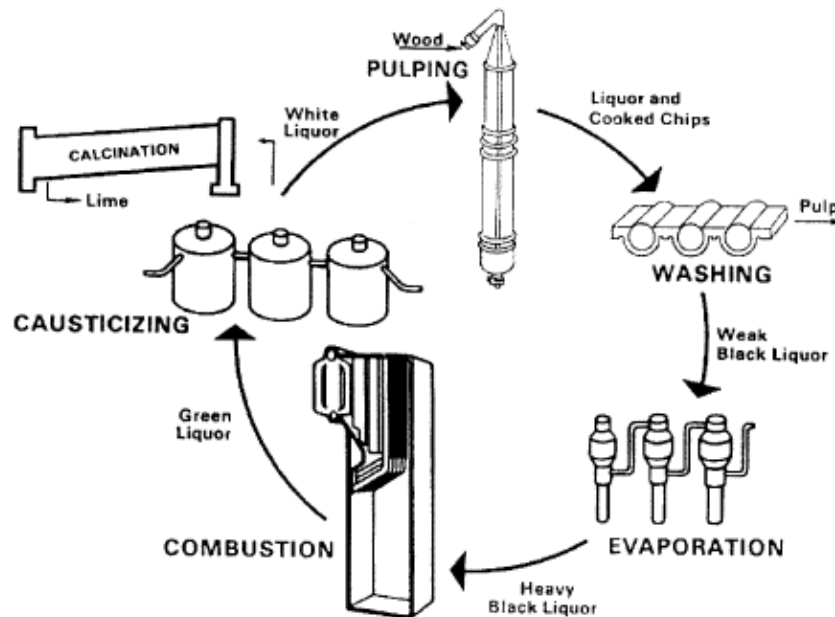
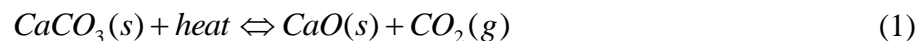


Fig 1. Causticizing process as part of the kraft pulp mill chemical recovery circuit. (Järvensivu et al. 2001, 590)

2.1 Function and construction of lime kiln

Lime reburning is part of chemical circuit called lime cycle. Lime regeneration is called reburning because it involves treating lime mud in high temperatures in a lime kiln. The function of the lime kiln is to convert lime mud back to lime for reuse in the causticizing process. Function 1 shows the conversion from lime mud to lime. (Gullichsen & Fogelholm 1999, B178)



Lime kiln is a rotary combustion kiln where heat transfers from combustion gas to lime particles. Lime kilns are typically 2-4 m in diameter and 50-120 m in length with typical rotation speed of 0.5-1.5 rpm. Lime mud is feed to the kiln from cold end and the kiln slopes slightly, about 1-4 per cent toward the firing end. Lime mud moves slowly at the bottom of the kiln towards the firing end as result of inclination and rotating. Flue gases and lime dust exists the kiln from the cold end. Flue gases pass trough electrostatic precipitator and wet scrubber and lime dust captured in the precipitator is fed back to the kiln. Lime retention time in the kiln is approximately 2.5-4 h depending on kiln

dimensions, rotation speed and lime mud properties. (Järvensivu et al. 2001, 630)

Figure 2 shows lime kiln at Iggesund pulp mill, Sweden.

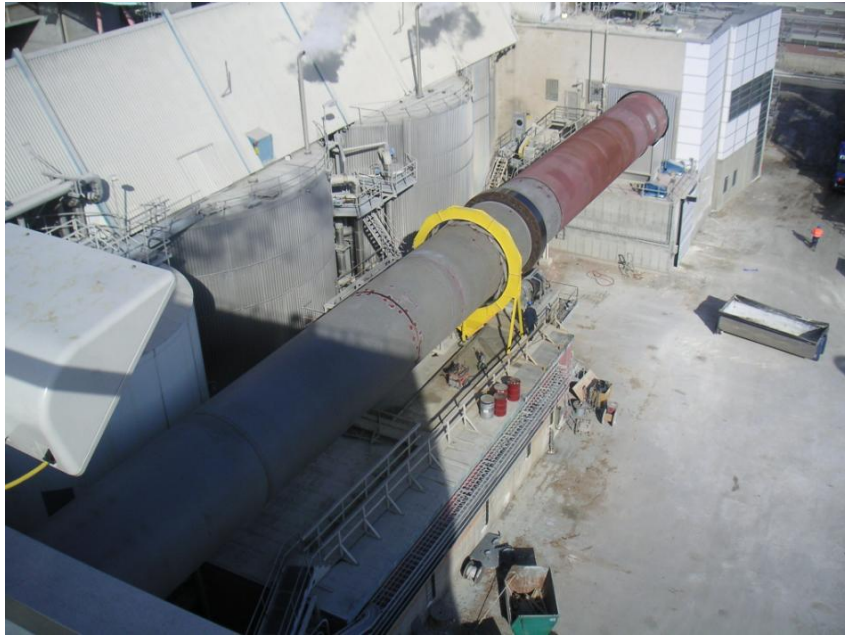


Fig 2. Lime kiln at Iggesund pulp mill. (Svedin et al. 2009)

Lime kiln can be divided to four process zones according to the temperature profile of solids and fuel gases:

- Thermal drying: moisture in the lime mud evaporates
- Heating: lime mud heats to the reaction temperature
- Calcination: calcium carbonate dissociates into calcium oxide and carbon dioxide
- Sintering and cooling: formed fine powder agglomerates into nodules and then cools before leaving the kiln

Figure 3 shows an example of cross-section and heating profile of lime kiln. Red line in the figure is fuel oil and blue line is biogas firing. Calcination reaction occurs in the actual burning zone where gas temperature increases to 1100°C. The endothermic calcination occurs spontaneously when lime mud reaches 800°C and sufficient reaction rate is reached approximately at 1100°C. The flue gas temperature needs to be

significantly higher because of the poor heat transfer in the kiln. Lime kiln can also have chain section in the drying zone of the kiln to improve heat transfer from flue gases to the mud. (Gullichsen & Fogelholm 1999, B180-181; Järvensivu et al. 2001, 591)

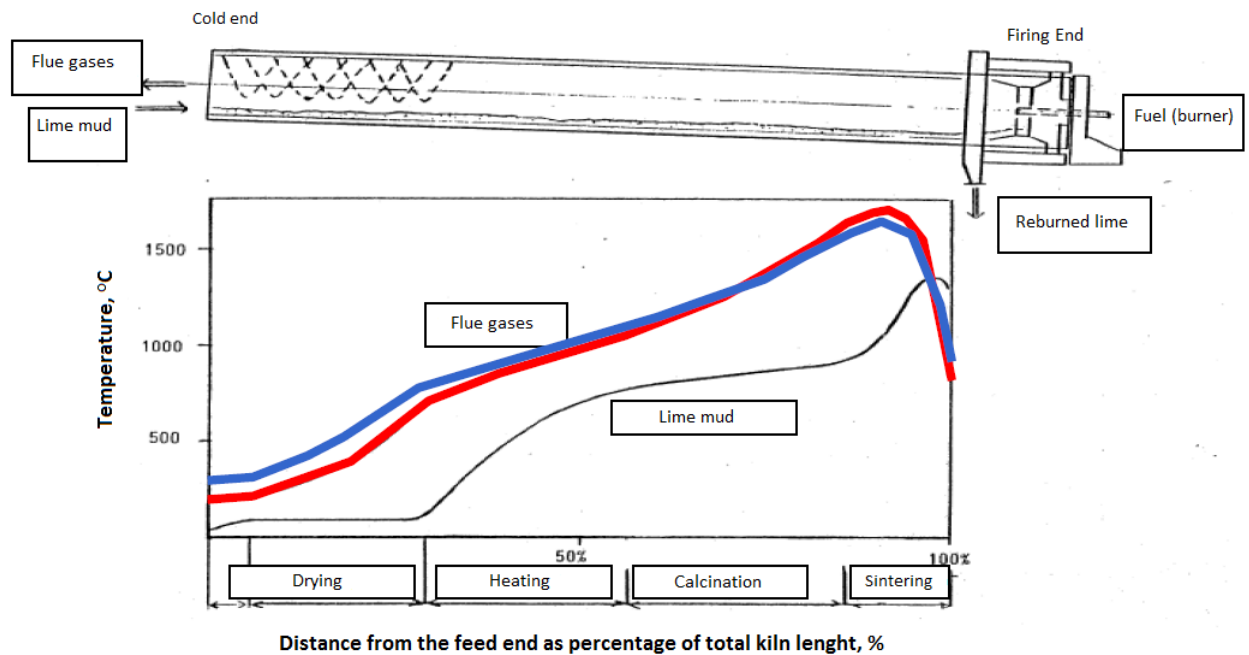


Fig 3. Lime kiln heating zones. (Isaksson 2007, original picture in Finnish)

Lime mud from lime mud silo is mechanically dried in filter plant before feeding it to the kiln. This is called lime mud dewatering and its purpose is to increase the dry solids in the mud. The moisture in lime mud has a significant effect on the energy consumption of the kiln. Dry solids content of 80 – 90% are often possible nowadays. (Gullichsen & Fogelholm 1999, B171)

Thermal drying of lime can be done with two alternative methods. Traditionally used method has been chain section of the rotary kiln with length of 20 % of the total kiln length. Nowadays pneumatic lime mud dryer (LMD) gives better energy efficiency and is therefore used more than the chain method. With no chain section kiln design is shorter and maintenance costs lower. In LMD dryer the lime mud is fed to a flue gas stream where the heat of the gases dries the mud. Then a cyclone separates dry mud and feeds it to the kiln. (Gullichsen & Fogelholm 1999, B182)

Lime mud has also to be sintered in the kiln to make usable product for further processing. In the final zone, lime powder agglomerates into lime nodules with diameter of 10-50 mm. (Gorog 2004, 8) Reburned lime is then cooled before leaving the kiln. Most kilns have a sector cooler attached at the end of the kiln where lime heat is recovered to combustion air. The burned lime from the kiln has a wide particle size distribution. Oversized particles are crushed by a lump crusher or hammer mill after leaving the kiln. (Gullichsen & Fogelholm 1999, B182)

All lime kilns have a refractory lining that protects kiln shell from overheating and limits heat losses. Refractory system consists of bricks that are composed of special heat-resistant and chemical-attack resistant materials, such as alumina or silica components. Each kiln zone has a lining of a certain material and thickness. Figure 4 shows arrangement for single-brick and two-brick lining in lime kiln. (Adams 2008, 2.2-3)

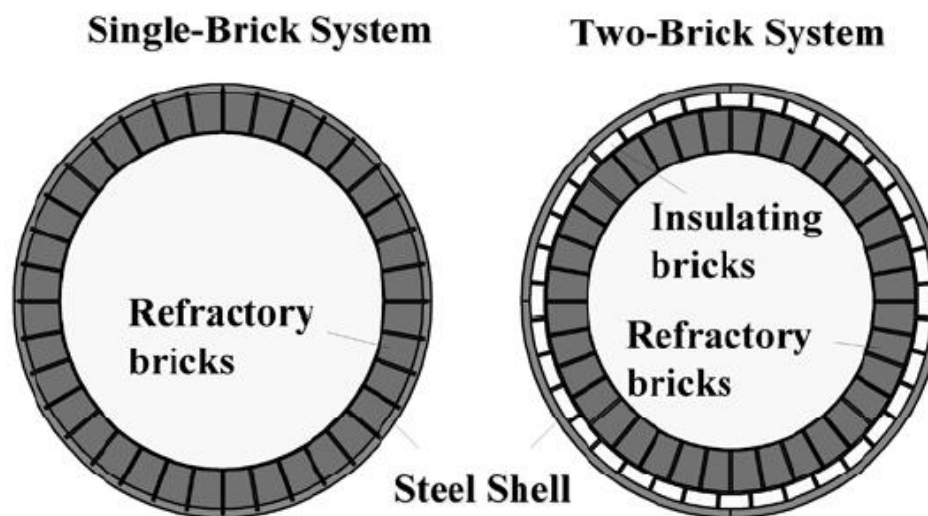


Fig 4. Example of brick linings in lime kiln (Adams 2008)

2.2 Typical fuels and carbon emissions

Modern pulp mill lime kiln can have production capacity of 500 tons lime per day. Treatment of lime mud in the lime kiln requires external heat and this requires high fuel combustion temperature. Higher flame temperatures mean higher production capacity and efficiency, but too high temperatures cause refractory damage and over-burned, slow-reacting lime product. Therefore stability and control of the combustion

temperature are also important to make good quality lime and to maintain stable operation of the kiln. (Adams 2008, 2.2-2)

Lime kiln fuel demand is 5.5-7 GJ per ton of CaO production. Main fuels used in lime kilns are heavy fuel oil or natural gas. Lime kiln is the biggest user of fossil fuels in kraft process and the only part of the pulp mill that needs substantial purchasing of fuel. Carbon dioxide (CO₂) emission from the kiln is directly proportional to the carbon (C) in the kiln gas. This comes from two sources: lime mud conversion and combustion of fuel. Two thirds of the carbon emissions come from the lime mud conversion and one third from the fuel combustion. Carbon in lime mud originates from wood and can be considered as carbon neutral. Carbon dioxide from fuel combustion has positive carbon footprint and if fossil fuels are used for combustion, they are counted as greenhouse gas (GHG) emissions. (Manning & Tran 2009, 3)

Lime kiln always needs some amounts of makeup lime to cover lime losses and lime containing impurities. Although losses of calcium from recovery system are usually made up using fresh lime, some amounts of make-up CaCO₃ are sometimes used in the kiln. Carbon contained in CaCO₃ is usually fossil origin and escapes as CO₂ from the kiln. This is also counted as fossil CO₂-emission. (ICFPA 2005, 25)

Rising and unstable price of fuel oil and natural gas has increased production costs in pulp and paper mills. Also possible tightening carbon emission limits and taxes for fossil fuels can increase the costs in the future. Therefore, there is a need for pulp mills to find more economical, carbon neutral alternative fuels that have minimal impact on lime kiln operation and chemical recovery process.

In late 2008, a large survey on lime kiln operation and fuel usage was made by TAPPI, the leading association for the worldwide pulp, paper, packaging and converting industries. Responses were received from 59 pulp mills from 9 countries totaling 67 lime kilns. Survey showed that about two thirds of the kilns have plans for implementing alternative fuels within the next five years. (Francey et al. 2011, 19)

Figure 5 shows that 16 kilns are using alternative fuels presently. Eight burn petcoke, six burn tall oil pitch, one burns olein biofuel and one burns biogas and tall oil pitch.

Petcoke is the only non bio-based fuel of these. Up to 26 kilns more are planning to use alternative fuels in the future.

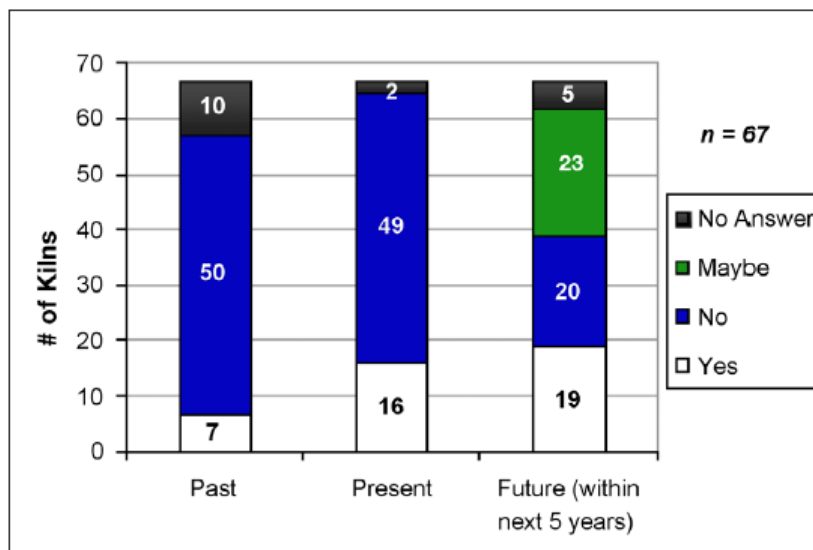


Fig 5. Past, present and future use of alternative fuels in lime kilns. (Francey et al. 2011)

Figure 6 shows that the most popular fuel considered for future use is biomass/biogas, followed by petcoke, bio-oil and lignin. Responses in other option included tall oil pitch and pulp mill waste streams tall oil, hydrogen, methanol and turpentine.

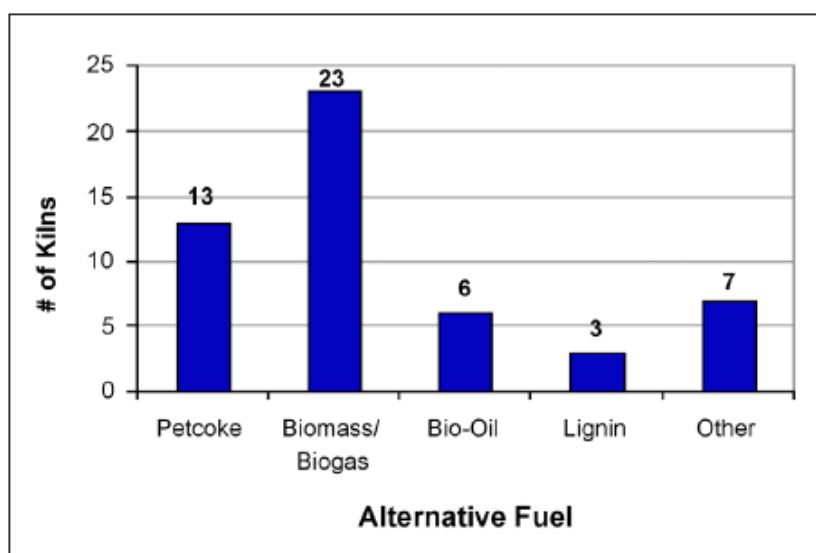


Fig 6. Alternative fuels being considered for future use. (Francey et al. 2011)

Figure 7 shows that the main motivations of alternative fuel use are lower energy costs and renewable energy. Responses in other option included avoiding fossil fuel CO₂ emissions, better kiln operation and biodiesel plant located next to the kiln.

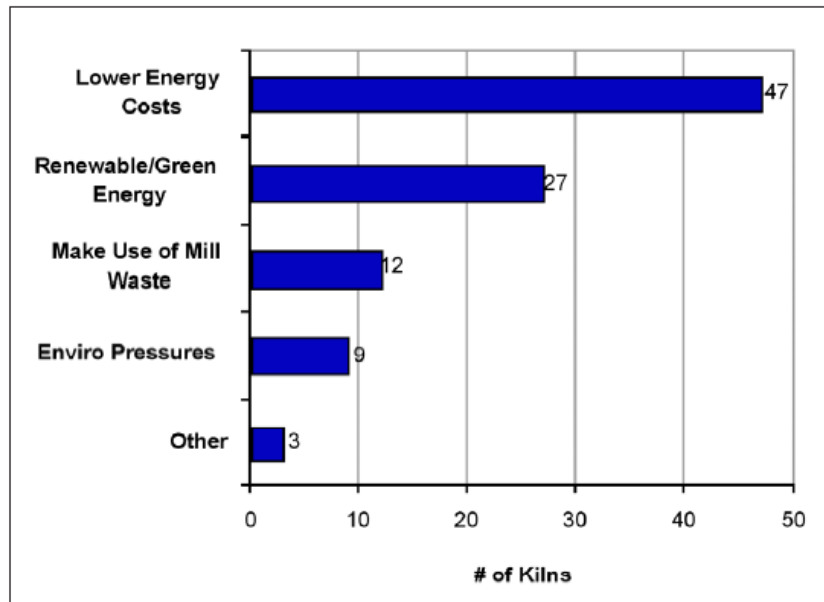


Fig 7. Main motivation for alternative fuel use. (Francey et al. 2011)

2.3 Other emissions and non-process elements

Also other emissions from the lime kiln process have to be controlled than carbon dioxide. Environmental authorities set emission requirements for sulfur dioxide (SO₂), total reduced sulfur (TRS), nitrogen oxides (NO_x) and particulates. Controlling emissions is much easier when knowing their sources. SO₂ forms in combustion of fuel when the fuel contains sulfur. TRS emissions consists primarily of hydrogen sulfide (H₂S) and may occur if the fuel contains sulfur and insufficient air is present for complete combustion. The main origin of H₂S is sodium sulfide in the lime mud fed into the kiln. TRS emission is usually low with proper mud washing. (Gullichsen & Fogelholm 1999, B194)

Particulate emission consists of lime mud dust and alkali. Lime mud dust carryover from the feed end can be collected almost totally with scrubber or electrostatic precipitator. Alkali dust formation is related to high temperature at the hot end of the kiln. Sodium compounds vaporize in the burning zone and condense to very small

particles. Alkali emission relates to lime mud washing. Sodium components are usually so small that electrostatic precipitator is necessary. Nitrogen oxides, which consist mainly of NO, always form during combustion if nitrogen (N) is present. Formation of NO_x starts when temperature is over 650°C and increases rapidly when it exceeds 1400°C. Burner design and adjustment of lime kiln temperature profile can avoid temperature peaks. (Gullichsen & Fogelholm 1999, B195)

Non-process elements (NPE) are impurities in kraft mill process steams. NPEs in the lime cycle come from green liquor, lime kiln fuel and makeup-lime. NPE levels are controlled by removing lime mud from the cycle. (Isaksson 2007, 8) Most impurities in the lime cycle usually come from green liquor. Quality of reburned lime depends heavily on the amount of impurities that enter the lime cycle via green liquor, and limiting the input of NPEs is the best way to maintain high quality lime. Many of NPEs are removed as dregs and green liquor filtering has given the best result in green liquor purification, decreasing required lime makeup to only 3%-5%. (Lundqvist 2009, 31)

Most typical NPEs in the lime cycle are magnesium (Mg), aluminum (Al), silicon (Si), iron (Fe), phosphorus (P), and sulfur (S). Impurities in the fuels fired in the lime kiln can mix with lime and part of those remains in lime cycle. It is important to ensure that minimum amount of NPEs are entering the lime cycle via fuel combustion. (Gullichsen & Fogelholm 1999, B149) That has been mainly problem when burning solid fuels in the kiln. High ash content in the fuel may increase NPEs, as ash itself is made from numerous compounds, some of which may influence the lime cycle. (Lundqvist 2009, 31)

3 ALTERNATIVE LIQUID BIOFUELS

In this section alternative liquid biofuels, that can be used for lime kilns are introduced. First the origin and availability of biofuels are presented, and then the properties of alternatives are compared to the heavy fuel oil and natural gas.

Biofuels are counted as carbon neutral fuels, and are usually free from carbon dioxide tax or energy tax. Also sustainability and ethical aspects should be taken into account when considering use of biofuels. Use of food crop based, first generation (1G) biofuels for energy production can have wide social impacts and increase food crisis in poor countries. Clearing of vegetation to make place for bioenergy plantations can result in indirect CO₂ emissions if large carbon stocks as dense rainforests are harvested. Use and harvesting of wood based biofuels can decrease habitat diversity and destruct landscapes.

Liquid fuels are easier to transport, handle and store than solid fuels. The energy density of liquid fuels is usually high which has positive logistic advantages. Also combustion properties and quality of fuel are usually more consistent than with solid fuel.

Combustion of other liquids than fuel oil is possible in the lime kiln and they can replace the primary fuel partially or totally. The burner design should use the same principles as oil burner, and water content must be well below 5% when replacing a high proportion of primary fuel. Proper atomization of fuel is necessary, and the flame stability must be secured. (Gullichsen & Fogelholm 1999, B192) Also multifuel burners, which can inject different types of fuel to the kiln are becoming more common. Figure 8 shows an example of Holcim multifuel burner with possibility to burn solvents, oil emulsion, waste oil, petcoke and saw dust.

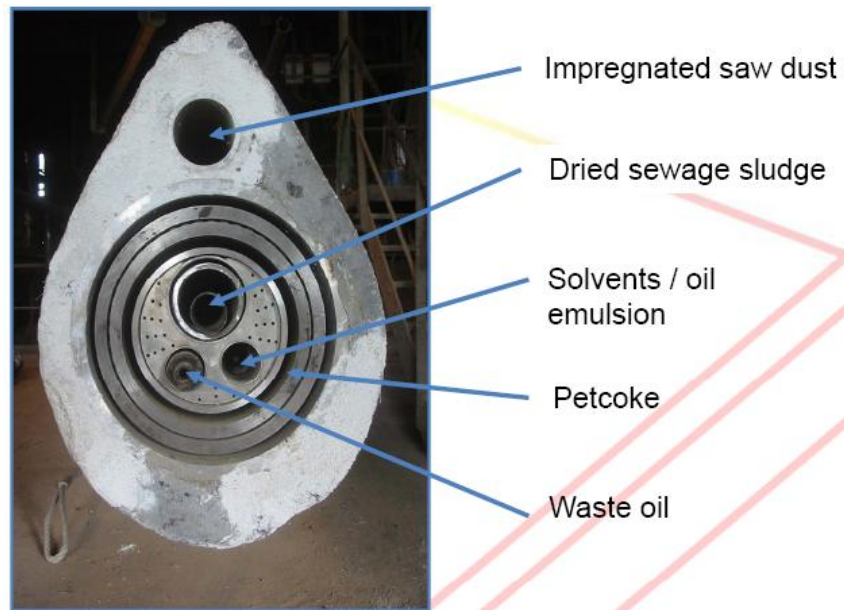


Fig 8. Multifuel rotary kiln burner. (Lowes 2009)

It is important to know some properties of the fuel like density, viscosity, heat value and adiabatic combustion temperature when examining handling and storing of the fuel and effects on combustion in lime kiln. Also chemical composition like ash-, sulfur- and nitrogen contents must be known when studying effects on causticizing process and flue gas emissions.

3.1 Vegetable oils

Vegetable oils can be extracted from a variety of different crops that grows all over the world. Usually oils are extracted from soya, oil palm or rapeseed, but nowadays there are also more unusual variants in the form of almond oil, hazelnut oil and cottonseed oil. (Sandgren et al. 2010, viii)

3.1.1 Crude Palm Oil

Palm oil is obtained from the fruit of palm tree, which grows well in hot and humid countries, the main ones being Malaysia and Indonesia. Palm oil has very large yield per hectare and it is the largest vegetable oil in world production. Fresh fruit branches of palm trees are collected and taken to crude palm oil mill where the fruits are crushed to produce crude palm oil. Crude palm oil is then usually taken to a refinery where it is

fractionated into lighter liquid fraction called palm oil olein and more viscous fraction called palm oil stearin. (UK Environment Agency 2010, 2)

Palm oil can be used as a fuel oil for heat production, but due to its relatively high melting point, it needs to be heated to reduce its viscosity before combustion. As the presence of proteins in palm tree fruits, combustion of unrefined palm oil has increased NO_x compounds in the flue gases. (UK Environment Agency 2010, 2)

3.1.2 Palm Acid Oil

Palm acid oil (PAO) is a by-product obtained from refining of crude palm oil. The refining involves either a physical or alkaline refining process. The alkaline refining process involves neutralisation with alkali such as caustic soda and one of the by-products of this refining type is soapstock. Acidification of soapstock using sulfuric acid gives palm acid oil. PAO is manufactured mainly in Malaysia and Indonesia and it has been used for soap making and distilled fatty acid production. (Agrotrade, 2011)

PAO is offered for global markets mainly by manufacturers from Malaysia, Indonesia, India and Thailand (Global trading Alibaba, 2012) PAO biofuel is manufactured for markets in Sweden, and can be used as renewable fuel for heat production. (Silmu, e-mail 9.1.2012.)

3.2 Fuels from the pulp mill

3.2.1 Methanol

Methanol is a by-product from the evaporation phase in kraft process. Main purposes of evaporation are to increase the dry solids content of black liquor and separate methanol, turpentine and soap which are generated in cooking phase. (Vakkilainen & Kivistö 2010, 58) Methanol is a volatile organic compound and can be present in contaminated condensates. Methanol can be stripped out using condensate strippers and be burned with non-condensable gases or as a liquid. (Tran & Vakkilainen 2008, 1.1-3)

Liquid methanol has been used as a partial fuel for lime kiln. Only limited amount of liquid methanol can be obtained from condensates. Typical amount used is 10-15% of the total heat input to the kiln. The combustion properties of methanol are sufficiently

similar as fuel oils, but the heat value is about half of the oils. Methanol must be feed to the kiln trough separate nozzle that can be part of the main burner or completely separate burner. (Gullichsen & Fogelholm 1999, B192) Liquid methanol produced in pulp mill and incinerated in lime kiln contains about 10-15 % water. (Vakkilainen, e-mail 1.3.2012)

3.2.2 Turpentine

Turpentine is one of the volatile oils that can be extracted from pine wood. Turpentine as methanol, can be collected as condensate from the cooking process. During the cooking of pulp, the turpentine contained in wood chips is volatiled and then condensated. The condensate contains crude sulfate turpentine (CST) which includes sulfur compounds. During further processing it is refined by fractial distillation and can be used as a solvent for pharmaceutical industry. (South Africa NEDLAC 2004)

CST is a mixture of α - and β -pinene and other monoterpenes and various impurities, such as unpleasant-smelling sulfur compounds and inorganic coumpounds. There are some safety risks associated with handling of CST and refined turpentine, due to its volatility and low flash point. (Wansbrough 2005, 1) Also turpentine has been used as a partial fuel for lime kiln in some pulp mills, typical amount is 10% of the total heat input to the kiln.

3.3 Terpene residue

Terpene residue is turpentine derivatives based liquid biofuel, manufactured in the USA. It is composed of terpenes, terpene alcohols and terpene polymers and is used as clean-burning substitute for fossil fuels. Terpene residue can be burned alone or in any mixture with residual fuel oils, and its high degree solvent acitvity improves the handling characteristics of mixture. (Silmu, e-mail 30.1.2012)

3.4 Crude tall oil pitch fuels

Tall oil is a valuable by-product of the pulp and paper industry. It is a mixture of mainly acidic compounds like turpentine found in pine trees. It is used as resin in many industries, including paper manufacture, paint manufacture and synthetic rubber manufacture. Tall oil is extracted at pulp mill. Black liquor from pulp making process is

concentrated and left to settle in tanks. The top layer formed is known as tall oil soap and is skimmed off. The tall oil soap is then reacted with acid to form crude tall oil (CTO). (Wansbrough 2005, 1)

CTO was used in some mills in Finland for heat production until taxes had to be paid for burning it starting 1.1.2007. Tall oil soap is also a possible liquid fuel for lime kiln. Some mills have used it and for example in Finland it is also tax free in the kiln use. (Rönnqvist, comments of the study 22.2.2012)

In refining process crude tall oil is then distilled into five components with different boiling points: heads, fatty acids, distilled tall oil (DTO), resin acids and residue pitch. These pitch and heads which cannot be utilized into sellable products can be used as a liquid fuel material for heat production. Typical pitch yield from tall oil distillation is about 25% of the total distillates. (Wansbrough 2005, 9)

3.4.1 Tall oil pitch 1

Tall oil pitch 1 is made from tall oil pitch and other tall oil distillates. Pitch fuels are already in use as low-sulfur replacement of heavy fuel oils mainly in power plants and lime kilns. Tall oil pitch 1 is produced in Finland, Europe and in the USA. (Silmu, e-mail 30.1.2012).

In Finland, UPM Pietarsaari pulp and paper mill is using tall oil pitch fuel as replacement for heavy fuel oil in the lime kiln. Fossil carbon dioxide emissions levels have gone significantly down with this substitution. (UPM Pietarsaari 2009, 9)

3.4.2 Tall oil pitch 2

Pine diesel oil is manufactured from crude tall oil in Sweden. Crude tall oil comes to manufacturer from pulp mills, and major by product from the process is pitch oil, a high quality tall oil pitch. The yield of pine diesel oil is 55% and pitch fuel 45% of the crude tall oil. Production capacity of pine diesel oil is 100 000 m³/a. Pitch fuel is returned to pulp mills and can be used for heat production. (Silmu, e-mail 30.1.2012)

3.5 Biomass pyrolysis oil

Biomass pyrolysis oil, also referred as bio crude or bio-oil, is produced by thermally pyrolysing the organic components of the biomass residues in a combustion reactor, in the absence of oxygen at about 400-500°C. Products of this pyrolysis process are char and volatiles, which are condensed to form bio-oil. Process conditions for pyrolysis of biomass are shown in figure 9. Bio-oil is dark brown liquid with a smoky odour and may be used as fossil fuel substitute for heat and power production. (Francey et al. 2008, 7)

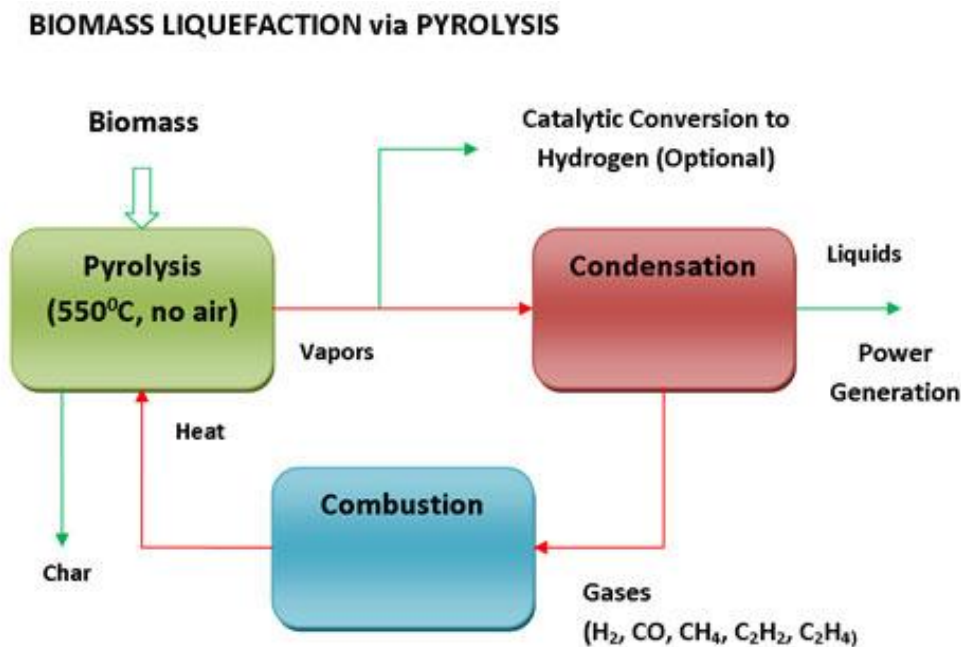


Fig 9. Process conditions for pyrolysis of biomass (Zafar 2011)

Virtually any source of biomass feedstock can be considered for pyrolysis, but most work has been performed on wood because of its consistency and comparability between the tests (Mohan et al. 2006, 848). Pyrolysis process is very dependent on the moisture content of the feedstock, which should be about 10%. At higher levels lot of water is formed and at lower levels there is risk that process produces only dust instead of bio-oil. Most of the pyrolysis technologies can only process small particles to maximum of 2 mm in diameter because of the need of rapid heat transfer through the particles. This means that the feedstock has to be dried and grinded to small particles before subjecting to pyrolysis. (Zafar 2010, 25)

Instead of building separate working pyrolysis process, it could be integrated to circulating fluidized bed (CFB) boiler which uses wood residues for heat production in pulp and paper mill power plant. Sand used for heat transfer in pyrolyser is taken from CFB boiler via pipe to a separate pyrolyser. Flue gases and charcoal formed in pyrolyser are then send back to the boiler for energy production. This integration is more cost-effective than separate pyrolysis process, from both operating and investment costs. This concept is called ITP (Integrated Thermal Process) and is mainly developed in Finland by Metso, UPM and VTT. (Brown 2011, 60) ITP process chart is shown in the figure 10.

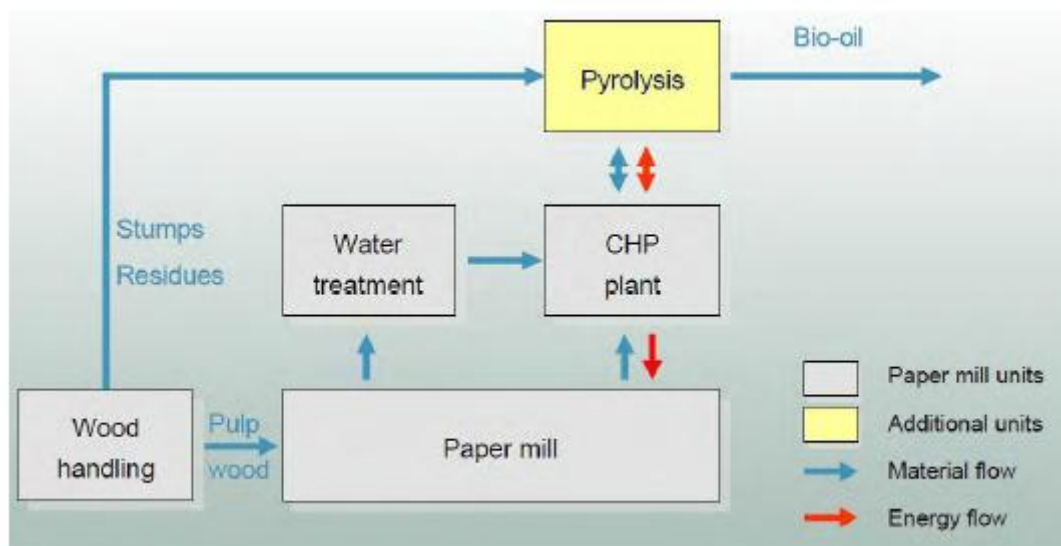


Fig 10. Thermal pyrolysis process integrated to paper mill. (Sohlström 2009)

At the moment, bio-oil is only used commercially in the food flavouring industry. However, bio-oil utilization has been proven and the European pulp and paper industry has potential to build up to 50 ITP-pyrolyzers. (Lehto, 2010) Bio-oil has been tested for lime kiln in small scale burning by using pilot lime kiln in University of British Columbia, Canada. Tests showed that bio-oil atomizes and burns well, yielding a flame similar to that of natural gas. Temperature and calcinations profiles were similar and lime reactivity was not affected. (Francey et al. 2008, 7)

3.6 Olein biofuel

Pulp mill in Brazil is currently burning filtered and liquefied animal fat in their lime kiln. Animal fat comes from a nearby meat processing plant, and the fuel used in the kiln is oil derived from it called olein. Olein is made up of fatty acids, but ultimately it consists mostly of carbon, hydrogen and oxygen. It has higher heating value almost same as heavy fuel oil. (Francey et al. 2008, 8)

The mill has conducted tests to characterize the fuel and through the temperature control they have managed to lower the viscosity of olein to the same as that of the heavy oil they were previously been using. They have also reported that the use of olein biofuel has reduced deposition in pipes, pumps and burners since it is more similar to light fuel oil than heavy fuel oil. The kiln operating has been comparable to that of using heavy fuel oil, and the mill is saving significant money on fuel costs. (Francey et al. 2008, 8)

4 EFFECTS ON LIME KILN

4.1 Emissions and handling

Available chemical compositions as weight percent in dry solids of fuels are gathered to table 1 from different sources. Table 2 shows combustion and handling properties of alternative fuels as received. Also same values are given from most commonly used kiln fuels, heavy fuel oil and natural gas for comparison. For this comparison is used low sulfur heavy fuel oil 180 which is used for energy and heat production in Finland. Further information about olein biofuel was not available at the moment.

Sources of the fuel data in the tables are: Crude palm oil (Guzman et al. 2010), Palm acid oil (UPM 2011), Methanol and Turpentine (Adams 2007), Terpene residue (UPM 2011), Tall oil pitch 1 (UPM 2011), Tall oil pitch 2 (UPM 2011), Pine pyrolysis oil (Alakangas 2000), Crude tall oil (UPM 2011), Heavy fuel oil 180 (Teboil 2009) and Natural Gas (Gullichsen & Fogelholm 2001).

It is important to note that composition and properties of biofuels depend on their raw material origin and the quality of fuels may vary a lot, if the biofuel is not a registered product. Therefore, fuel quality should be analysed periodically to avoid variations which may affect the combustion process. Also careful mixing of the fuels in their storage tanks has to be ensured if viscosity and density variations occur.

One of the major constraints on production capacity of the kiln is usually flue gas flow out of the kiln. If moisture content of the kiln fuel is high, formed water vapor decreases the production capacity. (Vakkilainen, e-mail 1.3.2012)

Methanol in the tables is produced at pulp mill and contains 15 % water. Turpentine in the tables is crude sulfate turpentine, also a by-product from pulp mill. Properties and moisture of pyrolysis oil depends on its raw material and pyrolysis technique. For this comparison is chosen pine pyrolysis oil with moisture content 20 % produced with fast pyrolysis process. Properties of crude tall oil and crude tall pitch oils depend on their raw material. In tables 1 and 2 is shown typical properties of crude tall oil and properties of tall oil pitch fuels from two different manufacturers. In the tables INA means that information was not available at the moment.

Table 1. Chemical compositions of fuels.

wt % dry solids	C	H	O	N	S	Ash	Moisture
Crude palm oil	INA	INA	INA	INA	0	INA	0.5
Palm acid oil	76	12	12	0.01	0.01	0.01	0.5
Methanol	37.5	12.6	49.9	0	0	0	15
Turpentine	83	12.2	0	1.6	3.2	0	0
Terpene residue	77.5	10.3	4.7	0.1	0.7	0.1	0.3
Tall oil pitch 1	81.9	11.4	5.8	0.1	0.3	0.3	0.1
Tall oil pitch 2	79.9	10.6	8.7	0.1	0	INA	INA
Pine pyrolysis oil	56	5.8	38	0.1	0	0.2	20
Crude tall oil	76.1	10.8	11.8	0.46	0.18	0.1	1.1
Heavy fuel oil 180	86	11	0	0.5	1	0.04	0.3
Natural Gas	74	24.5	0.1	1.5	0	0	0

Table 2. Combustion properties of fuels.

Properties	Lower Heat Value MJ/kg	Density, 15°C kg/m³	LHV per volume MJ/m³	Viscosity, 50°C cSt	Pour point °C	Flash point °C	Ad. Flame Temperature °C
Crude palm oil	38	914	34732	40	12	275	INA
Palm acid oil	39	900	35100	INA	35	200	INA
Methanol	16.6	796	13214	0.75	-97	13	2200
Turpentine	41.3	860	35518	40	-50	30	2100
Terpene residue	41.5	850	35275	4	-20	38	2100
Tall oil pitch 1	38	950	36100	470	15	150	2100
Tall oil pitch 2	INA	INA	INA	180	INA	INA	2100
Pine pyrolysis oil	17	1220	20740	25	-20	56	2000
Crude tall oil	36.9	940	36420	165	INA	190	2100
Heavy fuel oil 180	40.6	987	40072	165	-3	95	2200
Natural Gas	48.9	0.8	39	-	-	-	2100

Table 1 shows that palm acid oil and tall pitch oils have compositions most similar to heavy fuel oil. All liquid biofuels presented, except turpentine are virtually sulfur free, so TRS and SO₂ emissions shouldn't be a problem when firing them. Turpentine contains more sulfur than heavy fuel oil and can increase these emissions which can be a problem with new emission permits. Chemical composition of crude palm oil was not available.

Nitrogen contents of biofuels are small compared to fuel oil and natural gas. According to Kottila (2009), burning tall oil has resulted as lower NO_x emissions from the kiln. Exception is again turpentine with highest N content in the table 1 and practical experience has shown higher NO_x emissions from the kiln when firing it. Burner design and combustion stability is in important role in keeping NO_x emissions low.

Ash contents are close to zero with all biofuels and it is likely that no harmful amounts of NPEs are entering the kiln via combustion. Moisture contents are also low, which is also good for combustion. Exceptions are methanol with moisture content of 15% and pine pyrolysis oil with moisture content of 20%. Burning high amount of these fuels in the kiln form a lot of water vapor which may decrease the production capacity of the kiln. Ash content of crude palm oil and ash- and moisture contents of Tall oil pitch 2 were not available, but they are expected to be close to zero as in other similar products.

Pour point and viscosity plays a key role in handling and storing the fuels. The pour point of a liquid is the lowest temperature, at where it loses its flowing characteristics. If pour point of liquid is high, it may need some warming treatment during transport and storing. Viscosity is an internal property of fluid that offer resistance to flow. The lower the viscosity is, the better the liquid flows.

Liquid fuels are injected to kiln via burner nozzle. Required viscosity for atomization depends on burner design and the principle of atomization. Methods of atomization usually used are pressure atomization and steam/air atomization. Typical atomization viscosity is 10-20 cSt. (Gullichsen & Fogelholm, 1999, B191)

According to table 2, crude palm oil, palm acid oil and tall pitch oils have pour points 15°C or higher, so they need to be handled and stored warm in most countries. Especially palm acid oil with pour point of 35°C needs careful warming treatment to

avoid solidification. Tall oil pitch fuels have relatively high viscosities at 50°C, so they have to be preheated before entering the burner nozzle in the same manner as traditionally used heavy fuel oil. Also palm oils are likely to require some preheat treatment.

Methanol, turpentine and terpene residue have relatively low flash point and safety in transporting and handling them has to be taken into greater account.

4.2 Fuel requirement and effects on combustion

Amount of fuel needed for heat transfer in the kiln depends on heat value of the fuel. The heat value per unit volume is main property when estimating the fuel requirement. Table 2 shows calculated lower heat values per unit volume of fuels, according their densities at 15°C. Crude palm oil, palm acid oil, turpentine, terpene residue and tall pitch oils have lower heating value (LHV) per unit volume close to heavy fuel oil, so the fuel flow fed to kiln is only about 5-10% higher than as using fuel oil. Fuel flow using methanol or pine pyrolysis oil has to be 2 to 3 times the flow using fuel oil. Combustion properties of Tall oil pitch 2 were not available but they are expected to be similar with Tall oil pitch 1.

Some research and modeling are made to estimate fuel performance during combustion in lime kiln. The adiabatic flame temperature (AFT) and flame length are the dominant factors in determining lime kiln performance. Fuels with the same AFT have approximately same performance in the kiln. (Adams T. 2008, 2.2-1) Adiabatic flame temperatures of pitch oils and terpene residue in the table 2 are estimated based on the known adiabatic flame temperatures of tall oil and sulfate turpentine. Figure 11 shows an example of three types of rotary kiln flames.

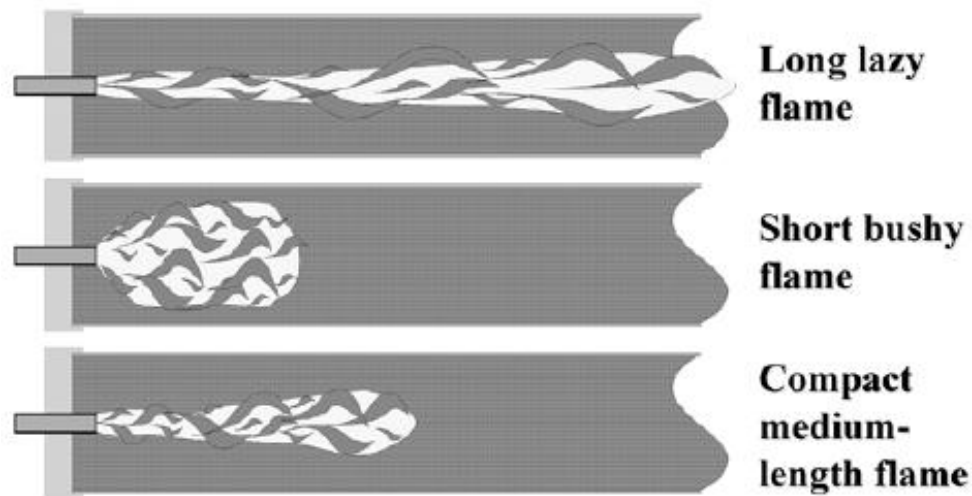


Fig 11. Rotary kiln flame shapes (Adams, 2007)

Short flames are too hot and can cause refractory damage and overburned lime. Long flames cause loss in production capacity and efficiency, and loss of control of the product quality. Medium flame about three times the kiln diameter in length is best option according to the efficiency and refractory service life. However the flame must not touch the refractory or serious refractory washing will occur. (Adams 2008, 2.2-2)

Recent simulation covered a range of solid, liquid and gas fuels operated at same excess air and production rate for each fuel. The kiln simulated was 3.3 m x 84 m kiln producing 240 tons lime per day. Table 3 shows results from the simulation of kiln performance for different fuels. (Adams 2007, 1)

Table 3. Results from the simulation of kiln performance for different fuels. (Adams, 2009)

	Adiabatic flame temp	Flame length	Feed end temp	Flue gas flow	Heat rate	Max refractory temp
	°C	m	°C	Nm ³ /h	GJ/t lime	°C
Conifer bark	2005	14.7	343	36,209	7.5	1449
Wood fuel	1982	14.9	354	36,780	7.6	1439
Peat	2007	14.8	344	36,273	7.5	1445
Lignin	2127	14.1	287	33,372	7.0	1487
Tall oil	2109	7.7	261	33,243	6.8	1700
Methanol	2108	7.7	251	32,689	6.7	1694
Tall oil pitch	1965	8.0	325	36,833	7.3	1617
Turpentine	2075	7.8	275	34,053	6.9	1678
Fuel oil	2068	7.8	280	34,256	6.9	1700
Bark fuel-gas	2226	13.2	244	31,033	6.6	1543

According to the table 3, flame length firing solid fuels is almost two times of that using liquid fuels. Flame length firing liquid fuels are approximately 80% of the optimal, medium length flame. Reducing primary air flow to the burner increases the flame length. This lowers the maximum refractory temperature in the firing zone significantly, while only affecting slightly to the other aspects of the kiln performance. (Adams 2007, 5) Also burner design affects to flame length in the kiln. As conclusion, flame length is not usually a problem when firing alternative liquid biofuels in the kiln.

4.3 Effects on kiln operation

Major issues causing severe problems in lime kiln operation are lime kiln ring formation, refractory damage, high dust load, TRS- and particulate emissions and poor lime quality. The most critical issue in kiln operation has been ring formation inside the kiln. These rings obstruct the movement of lime mud and may result in kiln shutdown for ring removal, causing major production losses. Several types of rings can form inside the kiln, but the most troublesome are mid-kiln rings that form in the middle of the kiln. (Lundqvist 2009, 6)

Figure 12 shows different types of kiln rings. Number 1 accords to dust ring, which occasionally forms during startups. Number 2 accords to mid-kiln ring and all lime reburning kilns have this ring. Number 3 accords to mud ring which can form if the

moisture content of lime mud leaving the chain section is more than 15%. Rings may form also in the burning zone of the kiln and ash content of the fuel may play a key role in burning zone ring formation. (Gorog 2002, 13)

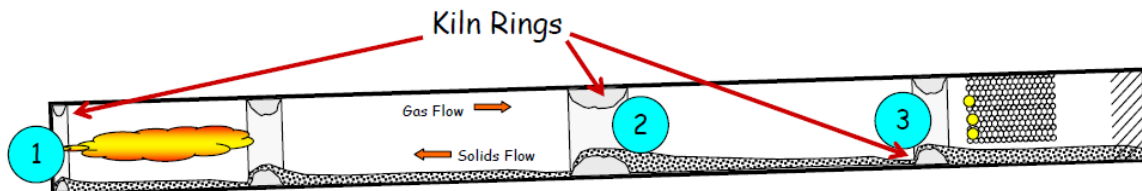


Fig 12. Location of kiln rings. (Gorog, 2002)

Mid-kiln rings form on the refractory lining by the same mechanism that forms nodules from lime mud. Small lime particles may stick to another to make nodules or to the refractory lining forming a ring. Initially the ring is soft and contains both CaCO_3 and CaO . If operation conditions change, the ring thickens and cools and CaO reacts with CO_2 to reform CaCO_3 . As this recarbonation occurs, the ring structure strengthens and the ring will no longer fall out by its own weight. The size of the mid-kiln ring depends on the sodium content in the mud and variability of the kiln operation. (Gorog 2002, 14)

Sodium (Na) usually has the highest concentration of NPE in the lime cycle and it has a tendency to accumulate inside the lime kiln. To control the ring growth, the total level of sodium content should be under 0.75 % in the lime mud. It is important to ensure that no harmful amounts of sodium is entering the kiln via fuel combustion or other ways. This means also balancing between lime mud wash and lime purge. Also lime production rate, fuel firing rate and amount of excess air impacts on kiln ring formation. Production rate has the greatest impact on ring formation and should be kept stable to avoid changes in operation conditions. Stability in the kiln operation is the best way to maintain consistent product quality. (Gorog 2002, 47)

Phosphorus (P) is present in the woodchips at the start of kraft process and comes to lime cycle with wood. P doesn't react at any stage of the kraft recovery process and it forms calcium phosphate by reacting with lime during the causticizing stage. Over the time calcium phosphate increases dead load in the lime cycle and has to be removed. Dead load in lime cycle increases internal energy use, chemical losses and operating problems. (Vakkilainen 2011, 55)

Typical Na content in heavy fuel oil 180 is 37 mg/kg. (Alakangas 2000, 136) In annex 1 is shown terpene residue chemical composition analysis, measured three times and in annex 2 tall oil pitch 2 chemical composition analysis, measured once. Both analyses are made by UPM-Kymmene Research Center, Lappeenranta. In annexes NPE contents of fuels are given by mg/kg. Annex 1 shows that Na content in terpene residue may vary a lot. Na contents of analysed fuels seem to be high compared to heavy fuel oil 180, in terpene residue average of three measures is 516 mg/kg and in tall oil pitch 2 is 213 mg/kg. Further analyses to measure the real Na contents of these fuels are recommended. P contents of these fuels are insignificant, in terpene residue 7 mg/kg and in tall oil pitch 0 mg/kg.

Sodium and phosphorus contents of liquid biofuels should not be a problem when firing them in the kiln. However periodical chemical analyses are necessary to examine the amount of NPEs in the fuels. Main things to secure stable kiln operation and to avoid ring formation when using liquid biofuels is to keep quality and properties of the fuels constant and the combustion process uniform.

5 TAXATION OF LIQUID FUELS IN EUROPEAN UNION

Taxation of fuels used in energy sector is one of the main things related to environmental policy and climate change strategy in the European Union (EU). Finland was the first country to introduce CO₂ tax for fossil fuels in 1990. (Heinimö, Alakangas 2006, 21) Other frontrunners launching CO₂ taxation were Sweden (1990), Norway (1991) and Denmark (1992). While concerns over climate change and new trend in energy policy spread, in the end of 1990s two of the largest EU economies Germany (1998) and UK (2000) introduced carbon-energy taxation too. (Andersen 2010, 2)

EU energy taxation is set in EU energy tax directive 2003/96/EC which came into force on 1.1.2004. In the directive are defined energy products and minimum levels of taxation for fuels. (Tullihallitus 2012, 1)

This section presents the fuel taxation in Finland, Sweden and Germany. Taxation of liquid biofuels and heavy fuel oil in these countries in industrial use is also compared. It is difficult to compare the energy taxation in these countries straight with each other, as the energy taxation systems vary and different tax regulations for fuels are used.

5.1 Finland

In Finland energy taxation is levied on electricity, coal, natural gas, peat, tall oil and liquid fuels. Excise tax of fuel is divided to energy content tax and carbon emission tax. All fuels have specific energy content and carbon emission taxes based on the properties of the fuel. In order to ensure security of supplies, additional security fee has to be paid for liquid fuels, electricity, coal and natural gas. All liquid fuels have specified security fees. (Tullihallitus 2012, 2)

Free from excise tax and security fee are fuels used as energy source in oil refining processes, fuels used in industrial production as a raw material or as an excipient, fuels used in the immediate first-use, other than in private pleasure craft used craft fuels, fuels used in electricity production, other than private pleasure-flying used fuels and liquefied petroleum gas. (Tullihallitus 2012, 3)

In pulp production fuels used in malodorous gas boilers and lime kilns are counted as immediate first-use but only if they produce a product and are part of the chemical

recycling process. If malodorous gas boilers and lime kilns are used only for combustion or heat production and chemicals are not recovered this is not counted as first-use. (Tullihallitus 2011, 8)

Therefore all fuels used in lime kilns are usually tax free in Finland. Exception is tall oil which is subject to tax in all combustion purposes. However energy-intensive companies can get tax refunds also from using crude tall oil, as explained later in this chapter. Fractions of tall oil, tall oil soap and tall oil pitch are tax free in lime kiln use. (Tullihallitus 2012, 3)

Table 4 shows taxation of heavy fuel oil, liquid biofuels and crude tall oil in Finland, in industrial heat production and in lime kiln use. Liquid biofuel in this context means heating oil produced from all types of biomass.

Table 4. Energy taxation of industrial heat production and lime kiln use in Finland. (Tullihallitus 2012)

Heat production	Energy content tax	Carbon emission tax	Security fee	Total tax
Industry	€/m³	€/m³	€/m³	€/m³
Heavy Fuel Oil	87,00	96,20	2,80	186,00
Liquid biofuel	77,00	80,00	3,50	160,50
Liquid biofuel R	77,00	40,00	3,50	120,50
Liquid biofuel T	77,00	0,00	3,50	80,50
Crude Tall Oil	176,60	0,00	0,0	176,60

Lime kiln use	Energy content tax	Carbon emission tax	Security fee	Total tax
	€/m³	€/m³	€/m³	€/m³
Heavy Fuel Oil	0,00	0,00	0,00	0,00
Liquid biofuel	0,00	0,00	0,00	0,00
Liquid biofuel R	0,00	0,00	0,00	0,00
Liquid biofuel T	0,00	0,00	0,00	0,00
Crude Tall Oil	176,60	0,00	0,00	176,60

In table 4 letter R means that biofuel meets sustainability criteria defined in the EU energy tax directive 2003/96/EC. Letter T means that biofuel meets sustainability criteria of the directive and has been produced from wastes or residues or non-edible cellulose or lignocellulose material. (Tullihallitus 2012, 5)

Energy-intensive companies, as pulp manufacturers can get tax refunds in Finland. When the total excise taxes of a financial year from electricity, coal, light fuel oil, heavy fuel oil, natural gas, crude tall oil and liquid biofuels and excise taxes included in the purchase price of these fuels are more than 0,5 % of the company's value-added, for the excess part the company has the right to apply for tax refund of 85% of the total excise taxes paid. From the tax refund calculated this way, only the part exceeding 50 000 € is paid. However the total tax refund may not exceed the total excise taxes paid from electricity, coal, natural gas and crude tall oil and excise taxes included in the purchase price of these fuels. When calculating the total excise taxes of a financial year paid, the company may take into account also the excise taxes in acquired district heating and process steam. (Tullihallitus 2012, 11)

5.2 Sweden

In Sweden there are energy taxes for electricity and fuels, for carbon dioxide and sulfur emissions and a levy system on nitrogen oxide emissions. The tax rate for fuels varies depending on whether the fuel is used for heating or as a motor fuel and whether it is used by industry or domestic customers. (Swedish Energy Agency 2011, 23)

Energy tax can be divided to fiscal tax and environmental tax. Environmental tax includes the carbon dioxide and sulfur taxes. General energy tax is essentially fiscal tax and it is levied on most fuels, based on various factors such as their energy contents. Carbon tax is levied on the emitted quantities of carbon dioxide from all fuels except peat and biofuels. Sulfur tax is levied per kg sulfur emission from coal and peat and for each tenth of one percent of sulfur by weight per cubic metre of oil. Oil containing less than 0.05 % sulfur is exempt from the tax. (Swedish Energy Agency 2011, 23)

Nitrogen oxides are levied per kg nitrogen oxides in emission from boilers, gas turbines and stationary combustion plants supplying at least 25 GWh per year. Nitrogen oxide levy is intended to be fiscally neutral and is repaid in proportion to each plant's utilized energy. Therefore only plants with highest level of emissions per utilized energy produced are the net payers. (Swedish Energy Agency 2011, 23)

Fuels used for heat production are equipped with energy tax, carbon dioxide tax and in certain cases sulfur emission tax and nitrogen oxide levy. Biofuels and peat used for heat production are tax free. Exception is crude tall oil which has high energy tax.

Industries that are not in the EU Emissions Trading System (EU ETS) have carbon dioxide taxation level 30% of the the general carbon dioxide tax level. Industries in the EU Emissions Trading System are exempted from carbon dioxide tax. (Swedish Energy Agency 2011, 23)

Table 5 shows energy and environmental taxes on industrial heat production in Sweden. Conversion from Swedish kronor to euros is made with finnish bank Nordea currency converter based on exchange rates in 8.3.2012.

Table 5. Energy taxation of industrial heat production in Sweden. (Swedish Energy Agency 2011)

Heat production	Energy content tax	Carbon emission tax	Sulfur tax	Total tax
Industry not in EU ETS				
	€/m ³	€/m ³	€/m ³	€/m ³
Heavy Fuel Oil	26,80	101,40	12,10	140,30
Liquid biofuel	0,00	0,00	0,00	0,00
Crude Tall Oil	128,20	0,00	0,00	128,20
Industry in EU ETS				
	€/m ³	€/m ³	€/m ³	€/m ³
Heavy Fuel Oil	26,80	0,00	12,10	38,90
Liquid biofuel	0,00	0,00	0,00	0,00
Crude Tall Oil	128,20	0,00	0,00	128,20

Energy-intensive industrial operations have special rules for fuel taxation. These rules allow a reduction of that part of the carbon dioxide tax which exceeds 1.2% of the retail value of manufactured products when 70% of the carbon dioxide tax has been deducted. A company is energy-intensive according to this rule if the remaining tax (excluding sulfur tax) after the general tax reduction for fuels used in heating amounts to at least 0.5 % of the value added by processing. (Swedish Energy Agency 2011, 24)

Tables 4 and 5 show that Finland has higher energy taxes for heavy fuel oil, liquid biofuels and crude tall oil in industrial heat production than Sweden. However all fuels except crude tall oil are tax free in lime kiln use in Finland. In Sweden replacing heavy fuel oil with liquid biofuel in lime kiln means money savings in energy taxes. Both countries have also tax refunds or tax reductions for energy-intensive industry.

5.3 Germany

In Germany energy taxes for light fuel oil, transportation fuels, natural gas and electricity contains excise tax, value-added tax and in some cases eco-tax. Fuels used for electricity production are excise tax free. (Energiateollisuus 2011, 81)

Heavy fuel oil has excise tax of 24,8 €/m³. However heavy fuel oil, natural gas and coal used in energy-intensive industry are usually tax free. Companies that make an agreement with the state to reduce emissions can get up to 95% reductions to their energy taxes in employer contributions. (Energiateollisuus 2011, 82)

Renewable energy sources act (EEG) is the most important legal instrument to promote electricity production from renewable sources in Germany. It offers fixed payments and remunerations for energy made from renewable sources. (Thrän et al. 2012, 7)

Liquid biofuels are mainly used in the transport sector of Germany. A further use of liquid biofuels like vegetable oils and biodiesel is for the generation of electricity and heat in compined heat and power (CHP) plants. Use of certified vegetable oil is required in order to be eligible for remuneration within the EEG from 2011 onwards. (Thrän et al. 2012, 29)

Taxation regulations for non-standard fuels, as the fuels discussed in this study, are very complicated in Germany. For each non-standard fuel the tax rate of a standard fuel which is the most similar in consistency and usage should be taken. Clearing sludge and rejects with average heating value under 18 MJ/kg are free from energy tax. (Bach, e-mail 19.3.2012)

As there seems not to be much liquid biofuels used in industrial heat production in Germany, the tax regulations for them are still unclear. Comparison to Finland and Sweden is very difficult without further studies about this issue.

6 CONCLUSIONS

Due to rising price of heavy fuel oil and natural gas and increasingly stringent environmental regulations in recent years, the interest in replacing these conventional fuels used in pulp mill lime kilns with biofuels has become a worldwide issue. Pulp manufacturers are looking both for money savings and nowadays increasingly important environmental reputation.

Fuels used for lime kilns have a lot of requirements compared to conventional combustion in heating boilers. As the operation of lime kiln requires lot of energy and affects to the whole chemical circuit of the kraft pulping process, the used fuel should have high heating value, good availability, constant combustion properties and should not contain much of nitrogen, sulfur and impurities. By knowing these requirements, replacing heavy fuel oil or natural gas with liquid biofuel is much easier and the operation of the kiln is predictable.

There are already both liquid and solid biofuels in use in some lime kilns. Practical experience has shown that liquid biofuels affect to the temperature profile and overall operation of the kiln less than solid fuels, compared to the kiln operation with heavy fuel oil or natural gas. Liquid biofuels also usually contain much less impurities and have higher energy density than solid biofuels, which is good for transporting, storing and handling.

There are already liquid biofuels in the markets, which has the required properties and can be used as energy source of lime kiln. All of the liquid biofuels examined in this study were more or less suitable for lime kiln fuel. The best options for primary replacing are wood based terpene residue and tall oil pitch fuels which have chemical compositions and combustion properties the most similar with heavy fuel oil. The raw material of these fuels can be obtained as by-product from the kraft pulping process. Tall oil pitch fuels have already been used in some lime kilns in Finland and Sweden. Mixtures of different kind of liquid biofuels are also interesting option in the future.

Also taxation regulations have impact on profitability of replacing conventional fuels with liquid biofuels. In most countries the taxes for fossil fuels in industrial use are much higher than for biofuels. However the straight comparison of liquid biofuel

taxation in different countries are complicated, as the countries may have many different national and regional tax regulations and tax reductions.

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ANNEX 1 Terpene residue analysis UPM

			Terpene residue	Terpene residue	Terpene residue		
10	Description		01/2011	02/2011	04/2011 (26/9/2011)		
11	Trialpoint					average	
12	LIMSno	Unit	Method	11-04392-001	11-04392-002	11-07264-001	
13	Sampling date			19.4.2011	26.5.2011	26.9.2011	
14	Parent id						
15	GC/MSD		Internal				
16	Density	g/cm ³	SFS-EN ISO 3675	0,9	0,9	0,9	
17	Aluminium, Al, ICP	mg/kg	SFS-EN ISO 11885	3,25	1,26	4,59	
18	Calcium, Ca, ICP	mg/kg	SFS-EN ISO 11885	13,1	9,84	53,6	
19	Cobalt, Co, ICP	mg/kg	SFS-EN ISO 11885	0	0	0	
20	Chromium, Cr, ICP	mg/kg	SFS-EN ISO 11885	3,33	1,44	0	
21	Copper, Cu, ICP	mg/kg	SFS-EN ISO 11885	0	0	0	
22	Iron, Fe, ICP	mg/kg	SFS-EN ISO 11885	34,1	11,2	54	
23	Potassium, K, ICP	mg/kg	SFS-EN ISO 11885	26,3	2,46	0	
24	Magnesium, Mg, ICP	mg/kg	SFS-EN ISO 11885	2,63	1,29	5,28	
25	Manganese, Mn, ICP	mg/kg	SFS-EN ISO 11885	0,84	0,366	2,4	
26	Sodium, Na, ICP	mg/kg	SFS-EN ISO 11885	1027	25,4	497	
27	Nickel, Ni, ICP	mg/kg	SFS-EN ISO 11885	6,52	3,92	40,7	
28	Phosphorus, P, ICP	mg/kg	SFS-EN ISO 11885	18,6	1,94	0	
29	Lead, Pb, ICP	mg/kg	SFS-EN ISO 11885	4,3	0,731	0	
30	Silicon, Si, ICP	mg/kg	SFS-EN ISO 11885	30,1	49,6	69,8	
31	Tin, Sn, ICP	mg/kg	SFS-EN ISO 11885	0	0	0	
32	Titan, Ti, ICP	mg/kg	SFS-EN ISO 11885	2,750	1,170	0,000	
33	Vanadium, V, ICP	mg/kg	SFS-EN ISO 11885	0	0	0	
34	Zinc, Zn, ICP	mg/kg	SFS-EN ISO 11885	3,91	0,987	31,9	
35	Sulphur, total (WIF)	Wt-%					
36	Nitrogen, total (WIF)	Wt-%	SFS -5505				
37	Ash 625°C (tall oil)	Wt-%	SCAN-T 4				
38	Water content, K-F	%	Internal	1,4	0,3	0,3	
39	Carbon residue	%	SFS-EN ISO 10370	1,38	0,10	0,21	
40	Flash Point	°C	SFS-EN ISO 2719	30,0	30,0	42,5	
41	Distillation of petroleum products		SFS-EN ISO 3405	Done	Done	Done	
42	Alfa-pinene, GC	Wt-%	Internal	5,1	6,2	7,9	6,4
43	Camphene, GC	Wt-%	Internal	1,2	2,4	1,8	1,8
44	Beta pinene, GC	Wt-%	Internal	5,2	12,0	7,1	8,1
45	Delta-3-carene, GC	Wt-%	Internal	1,2	0,6	1,3	1,0
46	Limonene, GC	Wt-%	Internal	16,7	6,6	10,4	11,2
47	Other C-10 terpenes, GC	Wt-%	Internal	9,3	23,9	8,9	14,0
48	Other terpenes 2, GC	Wt-%	Internal	19,6	28,9	17,9	22,1
49	Other high b.p. turpentine compounds, GC	Wt-%	Internal	18,4	6,6	29,2	18,1
50	Elution, GC	Wt-%	Internal	68,0	78,9	73,9	73,6
51	Total dry content, vacuum 60°C	%	Internal				
52							

ANNEX 2 Tall oil pitch 2 analysis UPM

Description			Tall oil pitch 2
Trialpoint			
LIMSno	Unit	Method	11-08589-001
Sampling date			
Parent id			
Aluminium, Al, ICP	mg/kg	SFS-EN ISO 11885	4,5
Calcium, Ca, ICP	mg/kg	SFS-EN ISO 11885	10,3
Cobalt, Co, ICP	mg/kg	SFS-EN ISO 11885	0
Chromium, Cr, ICP	mg/kg	SFS-EN ISO 11885	0
Copper, Cu, ICP	mg/kg	SFS-EN ISO 11885	0
Iron, Fe, ICP	mg/kg	SFS-EN ISO 11885	3,1
Potassium, K, ICP	mg/kg	SFS-EN ISO 11885	0
Magnesium, Mg, ICP	mg/kg	SFS-EN ISO 11885	0
Manganese, Mn, ICP	mg/kg	SFS-EN ISO 11885	0
Sodium, Na, ICP	mg/kg	SFS-EN ISO 11885	213
Nickel, Ni, ICP	mg/kg	SFS-EN ISO 11885	0
Phosphorus, P, ICP	mg/kg	SFS-EN ISO 11885	0
Lead, Pb, ICP	mg/kg	SFS-EN ISO 11885	0
Tin, Sn, ICP	mg/kg	SFS-EN ISO 11885	0
Titan, Ti, ICP	mg/kg	SFS-EN ISO 11885	0
Vanadium, V, ICP	mg/kg	SFS-EN ISO 11885	0
Zinc, Zn, ICP	mg/kg	SFS-EN ISO 11885	0
Resin acids	Wt-%	SCAN-T 14	33,0
Acid value	mg/KOH/g	SCAN-T 11	71,3
Carbon, C	%	ASTM D5291	79,9
Hydrogen, H	%	ASTM D5291	10,6
Nitrogen, N	%	ASTM D5291	0,1
Sulphur, S	%		0
Oxygen, O	%		8,7
Saponification value	g/l	SCAN-T 12	120,6
Unsaponifiables	Wt-%	SCAN-T 13	21,6
Viscosity, 25 °C	cP	Internal	1500,0
Viscosity, 40 °C	cP	Internal	400,0
Viscosity, 50 °C	cP	Internal	180,0
Viscosity, 60 °C	cP	Internal	75,0
Viscosity, 70 °C	cP	Internal	42,0
Viscosity, 80 °C	cP	Internal	23,0
Viscosity, 90 °C	cP	Internal	13,0
Viscosity, 100 °C	cP	Internal	9,0