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Degree Programme in Environmental Technology
Bachelor's Thesis

COMPARISON OF FORMALDEHYDE EMISSIONS DETERMINATION IN LIGNIN- AND PHENOLIC -BASED RESINS IN PLYWOOD PANELS

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Vaneriteollisuuden formaldehydipäästöjen mittausmenetelmien vertailu ligniini- ja fenolipohjaisilla hartseilla

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Hakusanat: ligniini-fenoli-formaldehydi hartsi, ligniini, vaneri, formaldehydipäästöt, kaasuanalysaattori, eksikaattorimenetelmä

Tässä kandidaatintyössä tutkitaan formaldehydipäästöjä mittaavien kaasuanalysaattorin sekä eksikaattorimenetelmien korrelaatiota. Tämän lisäksi työssä vertaillaan ligniini- sekä fenolipohjaisten hartsien formaldehydipäästöjä. Katsaus keskittyy vanerituotantoon ja tutkimus tehdään yhteistyössä UPM Biochemicalsin kanssa. Tällä hetkellä eksikaattorimenetelmällä mitatuille formaldehydipäästöille ei ole EN-standardia. Mittausmenetelmien välisen korrelaatiokertoimen avulla voitaisiin hyödyntää tätä kustannustehokasta ja helposti toteutettavaa mittausmenetelmää. Ligniini- ja fenolipohjaisten hartsien tutkimuksella kartoitetaan tulevaisuuden mahdollisuuksia formaldehydipäästöjen pienentämiseksi. Hartsityypin lisäksi kandidaatintyössä tutkitaan myös puulajin, liimanlevityksen sekä puristusajan vaikutusta formaldehydipäästöihin.

Kaasuanalysaattorin sekä eksikaattorimenetelmän tulosten välillä ei havaittu lineaarista korrelaatiota. Puulajin vaikutus formaldehydipäästöihin vahvistettiin, ja todettiin, että lehtipuut emittoivat vähemmän formaldehydiä kuin havupuut. Liimanlevityksellä ja puristusajalla ei havaittu olevan suoria vaikutuksia päästöihin. Myöskään hartsin ligniinimäärällä ei todettu olevan vähentävää vaikutusta vanerin formaldehydipäästöihin.

ABSTRACT

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Comparison of formaldehyde emissions determination in lignin- and phenolic -based resins in plywood panels

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31 pages, 11 charts, 10 tables and 5 appendices

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Keywords: lignin-phenol-formaldehyde resin, lignin, plywood, formaldehyde emissions, gas analysis method, desiccator method

In this bachelor's thesis, correlation for formaldehyde emission release measurments of gas analysis method and desiccator method was calculated. Also, formaldehyde emissions of lignin- and phenolic -based resins were compared. The study concentrated on the plywood panels and was carried out in cooperation with UPM Biochemicals. The correlation between methods was calculated for predicting the results. Today there is no EN-standard for formaldehyde emission limit values for plywood panels measured by desiccator method. Lignin- and phenolic -based resins were compared to study the future possibilities for formaldehyde emissions reduction. Other parameters studied in this thesis affecting the formaldehyde release were wood species, glue factor, and pressing time.

No linear correlation was found between the gas analysis method and desiccator method. It was confirmed that wood species tend to have an impact on the formaldehyde emissions in the panel. Hardwood emits less formaldehyde than softwood as it was predicted. Glue factor and pressing time were not detected to have a clear impact on the emissions. Also, the amount of lignin did not appear to reduce the formaldehyde emission from plywood panels.

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LIST OF SYMBOLS

A	area	[m^2]
d_i	spread	-
d_{ri}	percentage spread	[%]
k	coverage factor	-
l_x	width length	[m]
l_y	width height	[m]
l_z	width depth	[m]
n	number of replicates	-
R^2	correlation coefficient	-
s_{ri}	random error	[%]
U	expanded uncertainty	[%]
$\bar{x}$	average	-

Abbreviations

CO_2	carbon dioxide
FE	formaldehyde emissions
GHG	greenhouse gas
IARC	International Agency for Research on Cancer
LPF	lignin-phenol-formaldehyde
NaOH	sodium hydroxide
Na_2S	sodium sulfide
PF	phenol-formaldehyde
ppb	parts per billion
UF	urea-formaldehyde
VOC	volatile organic compound
WBP	wood-based panel
WHO	World Health Organization

1 INTRODUCTION

Formaldehyde is a pungent smelling, colorless compound, which is mainly used in producing resins with different components. These resins are used in wood production, molding materials, surface coatings, textile, leather, rubber, and cement industries. It is also used in producing other chemicals. This thesis deals with particularly phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) resin in the plywood industry. Formaldehyde is also formed naturally in troposphere from methane and occurs everywhere around us. It is to be known that formaldehyde emissions (FE) have an impact on people's health when exposed to large amounts. According to International Agency for Research on Cancer (IARC), the gas is a carcinogen to humans. (IARC, 2006, 45, 48, 94)

In this bachelor's thesis, formaldehyde emissions in plywood panels are observed by two determination methods which are desiccator (ISO 12460-4:2016) and gas analysis method (ISO 12460-3:2015). The main targets of this research are to find a possible correlation between these two methods, and also to compare FE of PF and LPF resins. Trial points of test samples are picked out precisely and the results are predicted to fluctuate according to the variables. Analyzable parameters are wood species, glue factor, hot press time and resin type. Study also includes error estimation. Thesis consists of theoretical and empirical research. The theoretical part takes a closer look at the determination methods that are examined in this research and observes the variables that may affect the results. In the empirical part of the report, the FE results are analyzed, and the possible correlation coefficient between two determination method is calculated. Also, comparison of LPF and PF takes place in that chapter.

The research is carried out with UPM Biochemicals, which is part of UPM-Kymmene Oyj -corporation. UPM is an employer of 18,400 people in a total of 46 countries. In 2019, total sales of UPM were 10,2 billion euros. The company is determined to strive towards carbon neutrality and managed to reduce CO_2 emissions by 6 % compared to the last year. UPM Biochemicals produce sustainable and innovative solutions in the field of wood-based biochemicals. The possible fields of use are bottles, textiles, packaging, composites, resins, deicing products, and functional fillers. (UPM-Kymmene Oyj, 2019, 10, 55, 138)

2 PLYWOOD PANELS AND RESINS

2.1 Plywood

Plywood panel is a rigid flat sheet made from wood by thin layers of veneer glued together. Veneers are glued with grain facing 90 degrees to the previous one, providing a strong final product. Veneers can be made from various kinds of trees. The final product itself can be a mixture of several types of veneer (combi) or one tree panel. UPM makes most of their veneers from birch and spruce. (WisaPlywood) In this study, birch and spruce panels are studied. Plywood panels have various end use possibilities as it is a strong and ecological construction material. The most common use for plywood panels is in construction, as it can be exploited widely from building’s framework to interior.

The manufacture of plywood starts with cutting the trees into shorter logs. Logs are then turned, getting one long piece of thin veneer. The veneer is cut into pieces either before or after the drying, this varies depending on the production line. After the veneer is dried and cut, it is time to sort different qualities from one another. Sorting is important because some of these veneers are too narrow or have holes in them. To save the material, this kind of pieces are filled and jointed. After refining, the veneers are ready to be glued and pressed. Application of the adhesive can be done by few different methods – with roller, curtain, foam extruder or spray coater. In the finishing part of the production line takes place sawing, sanding, grading, and packaging. (Koponen, 2002, 28, 67)

2.2 Phenol-formaldehyde resin

Resins are used in plywood manufacturing to make adhesive, the most common ones in the field are phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins. In this thesis, only the former is studied. Adhesive consists of hardener, water, and resin, and is formed in the mill site, according to the tailored recipe for each factory. The adhesive is ready for operation when the viscosity reaches the desired value. (Varis, 2019, 81-82) Resin plays an important role on the final product’s quality, as gluing of the veneers is one of the most crucial phases of the manufacturing (Koponen, 2002, 65).

Formation of PF resin happens with phenol and formaldehyde condensation, which is stopped halfway through the reaction. By adding alkaline catalyst, such as sodium hydroxide (NaOH), makes the product resol-type (Pizzi, 1983, 144). The condensation reaction of the resin is completed in the phase of hot pressuring, reaching the perfect hardening of the seam joint. PF resin-based adhesive’s recipe has remained almost the same since the 1950’s as it suits well for exterior use. (Varis, 2019, 135, 236)

2.3 Lignin

Lignin (figure 1) is a polymer, which is the second most abundant renewable resource after cellulose. It is one of the main components of plants, naturally occurring everywhere around us. In the branch of industry, it is possible to collect huge amounts of this nature’s product as it is a by-product in papermaking and bioethanol process. Lignin is the second major building material of wood with the composition ranging between 20 % - 30 %. Extraction of lignin is possible to be done under different circumstances affecting the features of the lignin and therefore the process of crosslinking to PF resin. (Pizzi, 1989, 155; Mancera et al., 2011, 2072; Alén, 2011, 33) This by-product is estimated to have a production capacity up to 50 tons per year, but 98 % of this lignin is utilized for energy (Kun and Pukanszky, 2017, 618).

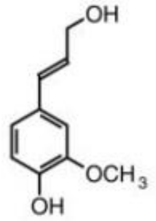


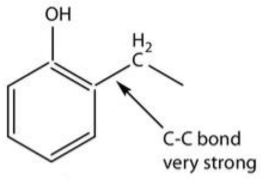
Figure 1. Chemical structure of one major monolignol (Hatfield and Vermerris, 2001).

Chemical modification of lignin is required as it is impossible to extract lignin from plants without one. The separation is done during another chemical process and lignin is usually just a by-product of the original process. Lignin extraction is possible to be carried out for example with soda, kraft, sulfite, organosolv process or steam explosion. In this thesis, only the kraft process is being observed as it is one of the commonly used pulping methods. The conventional kraft pulping is executed with sodium hydroxide (NaOH) and sodium sulfide (Na_2S). The cooking fluid is called white liquor and it assists the lignin to degrade. Outcome of the cooking is called black liquor and its dry mass contains 25 % to 31 % of lignin depending on the wood. (Kun and Pukanszky, 2017, 620-622; Alén, 2011, 76, 98) To reach a higher efficiency of the pulp mill, technology called LignoBoost can be utilized. Providing pure lignin with low ash content is done by evaporating black liquor and then lowering the lignin's pH with carbon dioxide (CO_2). Precipitated lignin is dewatered and then mixed with acidified water. For the slurry mixture to become so called lignin cakes, the slur is once again dewatered. (Valmet, n.d.)

2.4 Lignin-phenol-formaldehyde resin

Research in alternative adhesives has been done all over the world for quite a long time. In Finland for example, lignin-based adhesive called Karatex, was started to be made in the 1970's. Due to the low prices and rapid development of phenol-based resins, the lignin-based resin was prevented from large spread to the markets. (Varis, 2019, 135) The development and generalization of this kind of alternative is now more essential than ever. By replacing even some share of the phenol with lignin in resins, less fossil raw materials are consumed.

The environmental and economic aspects of this waste product make the raw material engaging. Native lignin (figure 1) is detected to have a similar structure as PF resins (figure 2). Cross-linking of LPF however requires longer pressing time and higher temperatures as to PF resins. (Pizzi, 1983, 254) These requirements and the modification of lignin reduces the effectiveness and increases the cost of this process. Due to low reactivity of lignin, increasing the lignin content above 30 % was not feasible for a long time. UPM is determined for heading towards bigger substitution rates and in 2013, UPM-Kymmene Corporation applicated for a patent to increase the reactivity of lignin. The invention showed that by treating lignin with alkalation, it is possible to reach a significantly higher substitution of phenol. This was a major step towards the goal as higher content of lignin have been successful since. (Pietarinen et al., 2014, 1)



1d

PHENOL-FORMALDEHYDE
RESIN

Figure 2. The chemical structure of PF resin (Kumar and Pizzi, 2019).

3 FORMALDEHYDE EMISSIONS

3.1 Formaldehyde

Formaldehyde (figure 3) is produced from methanol or methane by oxidation in the presence of a catalyst. The source for methanol is natural gas. Formaldehyde is widely studied and therefore is one of the best-known pollutants for indoor air. (Salthammer et al., 2010, 2537-2538) The compound is mainly used in producing resin with different components. These resins are used in wood production, molding materials, surface coatings, textile, leather, rubber, and cement industries. It is also a feedstock for producing other chemicals. (IARC, 2006, 45) In this study, only phenol-formaldehyde (PF) and lignin-phenol-formaldehyde (LPF) combinations in plywood production are being observed.

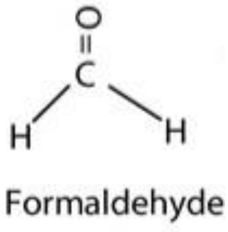


Figure 3. The chemical structure of formaldehyde (Kumar and Pizzi, 2019).

Formaldehyde is a natural compound as plants naturally contain formaldehyde, so the exposure outdoors is inevitable. The concentrations in the outdoor air differ greatly depending on the region. The value in the northern and central Europe, as well the United States, lies between 5 to 15 parts per billion (ppb) as to the cities with high photochemical air pollution has the average value between 20 to 30 ppb. Outdoor levels are however lower than indoor measures caused by the low air exchange indoors. The indoor emissions are difficult to define as there are so many factors affecting, but according to Salthammer (2013) the levels are roughly around 40 ppb. There are many potential sources for formaldehyde release indoor, for example, wood-based products, insulation, and coating materials. Also, combustion releases formaldehyde, which is a strong source in wood-heated homes. (Salthammer, 2013, 3323-3324; Salthammer et al. 2010, 2541-2542)

3.2 Guidelining the emissions

According to IARC, formaldehyde is a carcinogen to humans (IARC, 2006, 45). This has led to new regulations holding considerably lower exposure limits, in both workplace and nonoccupational environment. Nonoccupational limits are in general lower than the workplace ones. There are few ways for guidelining the formaldehyde emissions. One of the ways is by category, when health authorities establish exposure levels. The most common guideline used is by the World Health Organization (WHO). WHO has established a recommendation limit of 0,1 mg/m^3 (80 ppb) to short-term exposure indoors (WHO, 2010, 142). The second possible way for setting guideline values is by region. (Salthammer et al., 2010, 2551)

Material testing methods for formaldehyde emissions can be divided into two groups by determining the content or the release from the panel (Salthammer et al., 2010, 2549). In this study we are only observing gas analysis and desiccator method, which are introduced in the next chapter more closely. Both of these methods measure the actual formaldehyde releasing from the panel. According to the European standard EN 636, the interior panels must have a classification of E1 or E2. The exterior panels may not be classified. However, the approved methods for this classification are EN 717-1 (chamber method) and EN 717-2 (gas analysis). As desiccator method is not admitted for guidelining the plywood FE in Europe, the aim of this thesis is to find correlation between gas analysis and desiccator method. The correlation value would help predicting the FE from gas analysis method.

Standards for both limit values and measure methods are presented in table 1. The limits for formaldehyde release for wood-based panels by gas analysis determination are presented in EN 13986 standard. This European standard represents the panels used in construction. Classification is executed between two categories of E1 and E2. The Japanese Industry Standard JIS A 5908 gives limit values for panels determined by desiccator method. The possible classes are from one to four stars, four being the lowest release amount. According to Marutzky and Dix (2004), the Japanese F** is most equivalent to European class of E1 (cited in Salem, 2011). The relationship of these limit values are shown in the table 2 below. (Salem, 2011, 7-8, 81) Formaldehyde emissions of UPM plywood panels are however significantly below the guidelines (Seppänen, 2019).

Table 1. Standards and methods studied in this thesis.

Standard for limit values	**Determination method**
EN 13986	EN 717-2, ISO 12460-3
JIS A 5908	JIS A 1460, ISO 12460-4

Table 2. FE limit values for plywood in EN 13986 (gas analysis) and JIS A 5908 & 5905 (desiccator method).

	Gas analysis [mg/m^{2}h]	**Desiccator [mg/L]**	
		≤ 0,3	**F******
		≤ 0,5	**F*****
E1	≤ 3,5	≤ 1,5	**F****
E2	≤ 8		

3.3 Methods for reducing the emissions

Even if the formaldehyde emissions today were below the guidelines, the regulations are constantly tightening. Also, the environmental awareness and the concern for people's health demand actions for decreasing the emissions in the future. Formaldehyde is possible to be determined in different phases of adhesive's life cycle. The same goes with the emission reduction, as it is possible to concentrate on board production or on the subsequent emissions. In this thesis, the service life emissions are observed more closely. The methods studied for reducing FE are alternative adhesive, pressing time and glue factor. Also, the factor of wood species is discussed.

One of the factors affecting the FE is the species of wood. As mentioned above, plywood can be made of various kind of wood. In this thesis, we are only observing birch and spruce veneers. Weigl et al. (2009) declare that in general, hardwood species contain less formaldehyde than softwoods. The supposition is, that veneers made of birch emit less formaldehyde than veneers made of spruce. According to Böhm et al. (2012), emission values of birch truly are lower than spruce's ones – the exact values from the study are presented in table 3.

Table 3. FE values measured with gas analysis from solid wood.

Wood species	**FE values [mg/m^{2}h]**
Birch	0,049
Spruce	0,069

There are few known parameters affecting the emission rate that can be adjusted in the board production process. These adjustments are known to affect the FE during production, but not all the modifications have an impact on the subsequent emissions. During the press cycle, high moisture content slows the glue joint hardening reaction and causes more evaporation, which in turn increases the release of formaldehyde. According to Carlson et al. (cited in Johansson et al., 2002), the formaldehyde emissions increase with a longer pressing time and higher pressing temperature. The role of the glue factor is controversial. From one standpoint, more adhesive stands for higher emissions, but at the same time it can provide a tighter structure of the panel. Higher density in turn tends to keep the emissions confined and reduces the FE during production, but also in service life. This issue will be examined in the results chapter. (Johansson et al., 2002, 161; Chan Bao and Feng Hu, 2012, 97)

Reduction in both formaldehyde and greenhouse gas (GHG) emissions are possible to achieve by alternative adhesives. Formaldehyde used in resins today is manufactured via synthetic gas. Production of formaldehyde might however be done utilizing biomethane, which could be both economic and ecological option compared to traditional one (Singh, Devnani and Pal, 2016, 467). Alternative adhesives can be made by replacing traditional components by polyisocyanates or natural resources, such as tannin, lignin or vegetable proteins (Chan Bao and Feng Hu, 2012, 98-99). In this thesis, only lignin-based alternative is studied. Alternative adhesives offer a broad platform for research to move towards more sustainable wood-based panel (WBP) production in the future.

One method for decreasing the subsequent formaldehyde release is post-treating the panels, for example by coating or sealing the edges. However, in this case, other volatile organic compound (VOC) emissions should be taken into consideration. (Chan Bao and Feng Hu, 2012, 98-99) Under consideration should also be the other possible impacts of these modifications. Using these alternative compounds do not make the product yet biodegradable and the disposal remains challenging. The manufacturing of these panels should be economically sensible, and all the alternatives mentioned above are today not as competitive in terms of production as the chemicals currently used. Harnessing these alternatives for industrial use demand resources.

4 DETERMINATION METHODS

Determination methods that are studied in this thesis are desiccator (ISO 12460-3:2015) and gas analysis method (ISO 12460-4:2016). Both methods test the actual formaldehyde release from the panel by measuring the quantity of emitted formaldehyde absorbed in water. The major practical differences between these methods are the time required for the determination and the cost of the equipment. Both determinations are carried out in duplicate, and if differences in the average results over 20 % occur, also third tests should be carried out. In this chapter, both methods are studied more closely.

4.1 Gas analysis method

The European standard ISO 12460-3 represents the method of gas analysis, also referred as EN 717-2. Determination of formaldehyde with gas analysis method is taken place in a closed chamber with air temperature of (60 ± 0,5) °C and relative humidity of ≤ 3 %. Throughout the testing, the chamber is to maintain an overpressure of (1100 ± 100) Pa. The chamber's airflow of (60 ± 3) L/h is led from the chamber into paired wash bottles (figure 4). The air contains the formaldehyde from the test pieces. FE from test pieces is measured for 4 hours. A new series of wash bottles are replaced with the old ones every hour. The actual content of the formaldehyde is determined photometrically. Content of the formaldehyde is given in mg/m^2h.

Figure 4. Wash bottles of gas analysis method (Kumar and Pizzi, 2019).

In gas analysis method, test piece dimensions are (400 ± 1) mm × (50 ± 1) mm × board thickness. Three test pieces for this determination is needed. The edges of the test piece must be sealed, and the unsealed area shall be calculated. The board thickness does not have an impact on the emitting surface area as the edges are sealed. The target for total emitting surface area is 0,04 m^2. Example calculation for the surface area is shown down below (equation 1).

$$
\begin{aligned}
A &= l_x * l_y * 2 \qquad (1)\\
A &= (400\,mm * 50\,mm) * 2\\
A &= 40000\,mm^2 = 0{,}04\,m^2
\end{aligned}
$$

Gas analysis method today has a new standard (ISO 12460-3:2020), but in this thesis, the determination was executed by the norms of the old one because of the timeframe. The biggest adjustment in the new standard was test period changing from 4 hours to 3 hours, which makes the method even faster to execute. Despite the fact that the duration of this measurement is short, this method requires a great investment in equipment. This can be considered as a disadvantage of this method.

4.2 Desiccator method

The second determination method studied is desiccator method, which is represented in the European standard ISO 12460-4. The absorption of formaldehyde is carried out with (300 ± 1) ml of water at (20 ± 1) °C. The water dish is placed at the bottom of the desiccator and the test pieces on a wire mesh above the dish (figure 5). Emissions are kept confined for 24 h ± 10 min in the desiccator. However, before the actual testing, test pieces should be conditioned for 7 days. This is considered as a disadvantage of this determination method. This passive testing method do not require high-cost investments and is therefore more feasible. As in gas analysis method, the actual content of the formaldehyde is determined photometrically. Content of the formaldehyde is given in mg/L.

Figure 5. Desiccator method (Kumar and Pizzi, 2019).

In desiccator method, the test piece dimensions are (150 ± 1) mm × (50 ± 1) mm × board thickness. The target for total emitting surface area is 0,18 m^2. The number of the test pieces depend on the surface emitting area of one individual piece. By increasing the amount of test samples, it might be possible to reach a closer value for target emitting area. Example calculation for the surface area is shown down below (equation 2). The calculation represents 5-ply spruce plywood with board thickness of 15 mm (appendix I). The dimensions of these particular test piece are therefore 150 mm × 50 mm × 15 mm.

$$A = (l_x * l_y + l_x * l_z + l_y * l_z) * 2 \tag{2}$$

$$A = (150\,mm * 50\,mm + 150\,mm * 15\,mm + 50\,mm * 15\,mm) * 2$$

$$A = 21000\,mm^2 = 0{,}021\,m^2$$

The emitting surface area of one test piece differs greatly from the target value. The total amount of required test pieces is calculated down below (equation 3). The final emitting surface area is achieved by multiplying the individual value by the amount of the test pieces.

$$x * A = 0{,}18\,m^2 \tag{3}$$

$$x = \frac{0{,}18\,m^2}{0{,}021\,m^2} = 8{,}57 \approx 9$$

5 ANALYZING METHODS AND ERROR ESTIMATION

5.1 Correlation between methods

One of the main targets of this thesis is to find a correlation coefficient for formaldehyde emissions determined by gas analysis and desiccator method. This is done by utilizing the results from the test pieces. The correlation between determination methods is studied through linear correlation. Correlation value of at least 0,7 is considered as a strong correlation (Ratner, 2009). Correlation coefficient is first looked at as an overall review. As presented in table 3, wood species tend to have an impact on the formaldehyde emissions itself. For this reason, correlation value is also calculated with birch and spruce separately. Based on wood species observation, it is possible to tentatively infer, does this parameter affect the FE from the panel and is the correlation more reliable individually.

5.2 Adjustments for FE reduction

The hypothesis for adjustments to reduce formaldehyde emissions (table 4) are gathered from various literature. The assumptions are confirmed or repealed by analyzing the test results in the next chapter. The results are studied separately by both methods. Glue factor and pressing time are analyzed through linear correlation. Wood species and adhesive parameter are observed generally.

Table 4. Hypothesis for FE reduction.

Parameter	Adjustment for reduction of FE
Glue factor	Less adhesive
Wood	Hardwood over softwood
Pressing time	Longer pressing time
Adhesive	Lower molar ratio (less formaldehyde)

One of the main targets of this thesis is to compare the FE from the plywood panels made with PF and LPF resins. This is done by visual observation of bar charts. From table 4 it is possible to infer that with smaller molar ratio, the release of formaldehyde is also lower. The amount of formaldehyde in the resin varies by recipe. The comparison between LPF and PF is done to see, is there any correlation between the amount of lignin in the resin and formaldehyde emissions (molar ratio).

5.3 Error estimation

Error in measuring process can be caused either experimental or observational aspects. Observational error in turn can be divided into systematical error and random error. In this thesis, only random error is considered. Random error is unpredictable and impossible to eliminate from the measurement. It is caused by the environmental conditions and measuring instruments. Random error is calculated for both of the methods separately.

Calculations for random error in determination methods are done by using the formaldehyde release results from the panel, which includes the background concentration. The percentage spread of the result is calculated using spread and the mean of the measurement results. This in turn is used calculating the actual random error. Example calculation for random error in gas analysis method is presented down below (equation 4).

$$d_{ri}(\%) = \frac{d_i}{\bar{x}} * 100 \tag{4}$$

$$s_{ri}(\%) = \sqrt{\frac{\Sigma[d_{ri}(\%)^2]}{2*n}}$$

$$s_{ri}(\%) = \sqrt{\frac{3165{,}14\ \%}{2*42}} = 6{,}14\ \%$$

Gaussian normal is used to calculate the expanded uncertainty. With the confidence level of 95 %, the coverage factor k is 2. The calculation for expanded uncertainty of 95 % for gas analysis method is shown down below (equation 5).

$$U = k * s_{ri} \tag{5}$$

$$U = 2 * 6{,}14\ \% \approx \pm\ 12\ \%$$

Equations 4 and 5 are widely used in estimating the error in measuring in general. More precise calculations are shown in appendix II for gas analysis method and in appendix III for desiccator method. All results for error estimation are presented in table 5.

Table 5. Random error and expanded uncertainty for both determination methods.

	Gas analysis method	**Desiccator method**
Sri	6,14 %	17,78 %
U	12 %	36 %

The uncertainty of desiccator method is significantly higher than the gas analysis one. This can be taken under consideration in the results chapter when comparing the FE levels. Error estimation supports in assessing the reliability of the results and making conclusions.

6 RESULTS

There were total of 42 test pieces for both determination, which are analyzed in this chapter. Both measurements were carried out in duplicates. Measurements were performed by UPM-Kymmene Oyj. More specific description of the samples is to be found in appendix I. In the chapter 6.1, correlation coefficient is calculated for testing methods. Parameters affecting the formaldehyde emissions are studied in the chapter 6.2. Analyzable parameters are wood species, glue factor, pressing time and resin type. Formaldehyde emissions of LPF and PF resins are compared in the same chapter.

6.1 Comparing testing methods

All the results from both determination methods are presented in figure 6. This gives an overview from the correlation between methods. As can be tentatively seen from the figure 6, there is no clear correlation between methods. The drop in emissions at the end of the graph is caused by the wood species changing from spruce to birch. More precise observation is seen in figure 7.

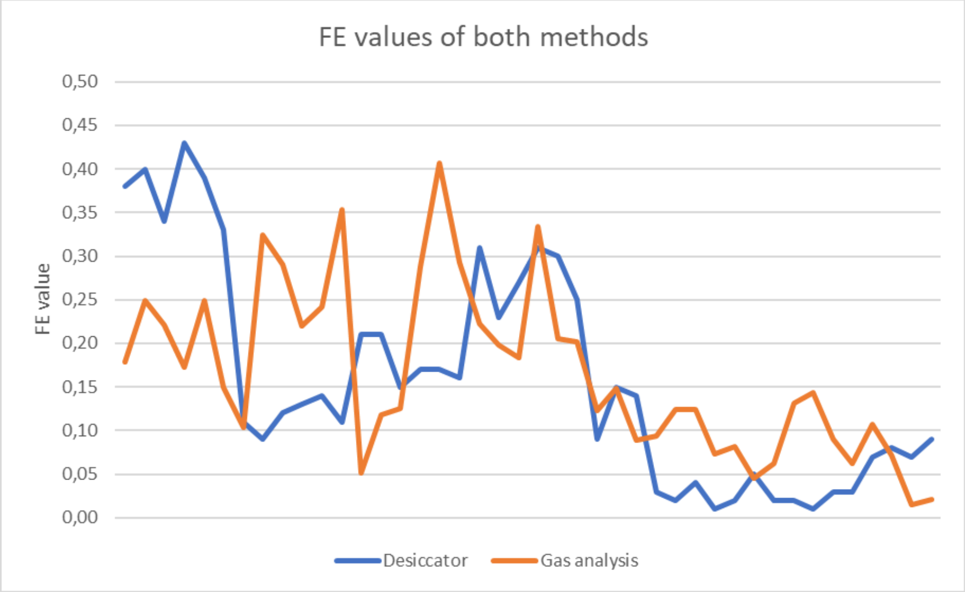


Figure 6. FE values of both methods.

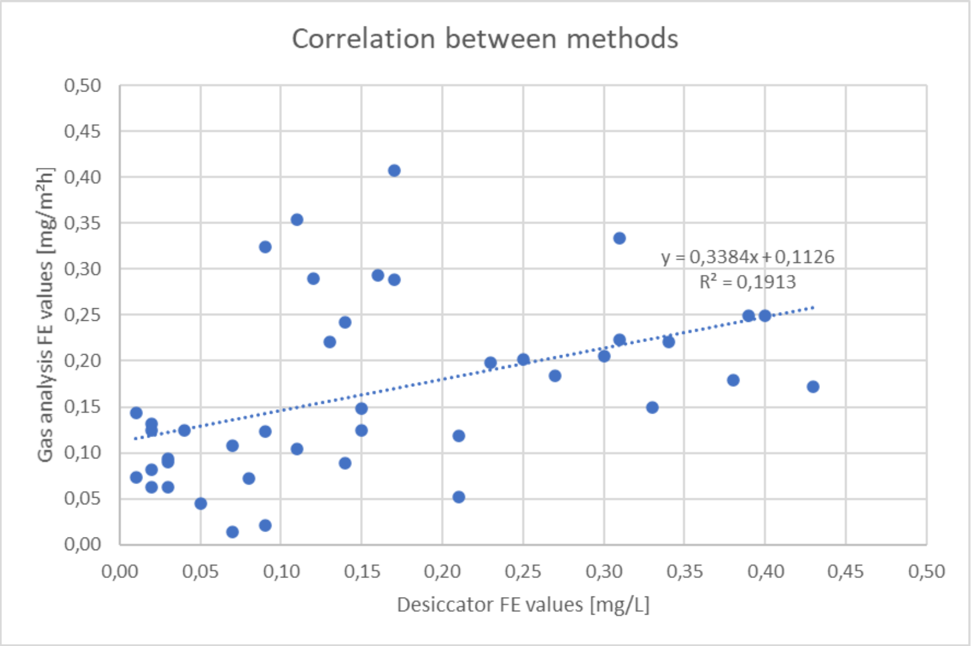


Figure 7. Correlation between determination methods.

Wood species is estimated to have an impact on the FE (table 3) and therefore both wood species are studied also individually (figure 8 and figure 9). As seen in table 6, the correlation with both wood species is significantly better than the correlation individually. A closer observation with certain variable gives a more decent outcome. This means, that in this case, study based on wood species is more reliable. The difference in the magnitude and the sign of the slope between overall and individual results cause contradiction. It is possible to infer that wood species in the same chart manipulate the results. It is also confirmed that the wood species have an impact on the FE from plywood panels.

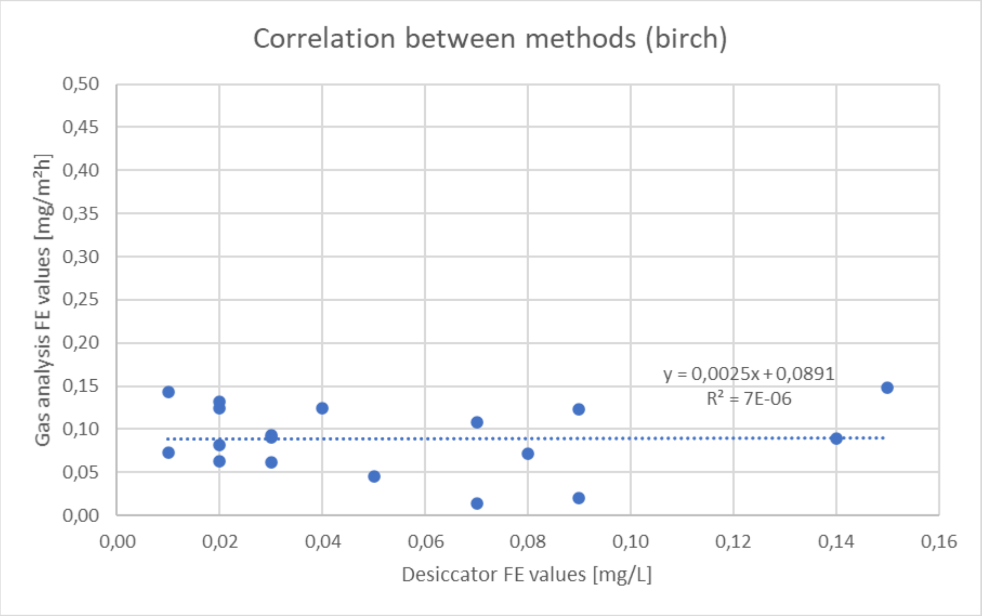


Figure 8. Correlation between determination methods for birch plywood.

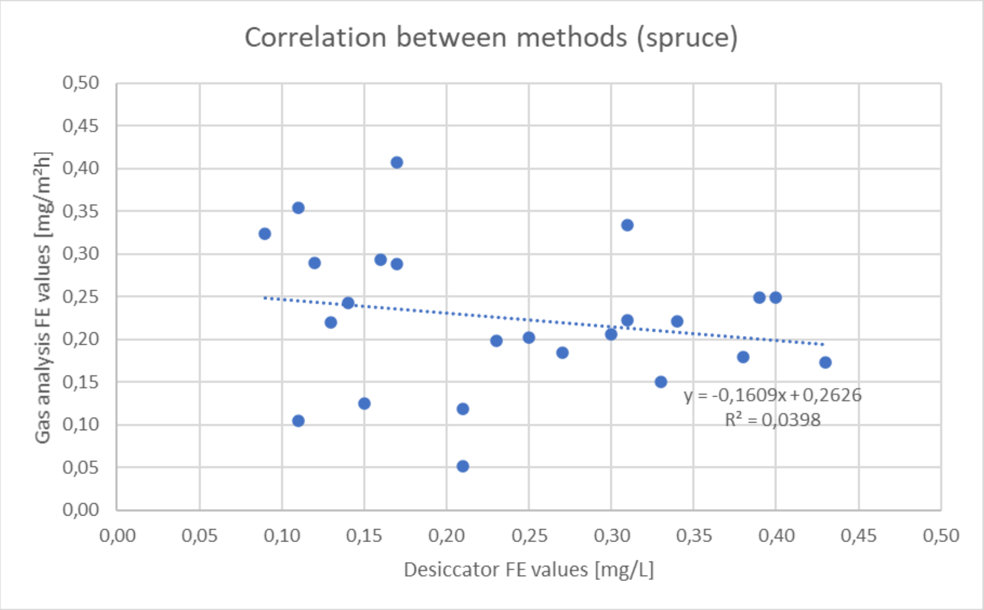


Figure 9. Correlation between determination methods for spruce plywood.

Table 6. Correlation coefficient (R^2) between determination methods.

Birch and spruce	0,1913
Birch	$7*10^{-6}$
Spruce	0,0398

6.2 Comparing the emissions of PF and LPF resins

Tables 7-9 present the results from appendix IV and appendix V. As noticed, the overall results including both wood species have a higher correlation coefficient with every variable than the individual ones. In this study, only the pressing time correlation with desiccator method gives a result for strong correlation. However, this scenario was already presented in the chapter 6.1, where conclusion of wood species manipulating each other was also drawn. For these reasons, this correlation is not considered as a relevant correlation.

By taking tables 8 and 9 under a closer investigation, it is possible to see that no reliable correlation is detected between the value of formaldehyde emissions and glue factor or pressing time. Only plywood made out of spruce reaches a pressing time correlation of 0,6833 measured by desiccator method (table 9), which is the closest to the limit value of 0,7. However, the correlation with gas analysis in the same situation is only 0,0687 (table 9). If the actual correlation would exist, the gas analysis value would also be significantly higher. Also, the expanded uncertainty of gas analysis is much smaller than the desiccator method one, which makes the former method more reliable and confirms the result of no correlation being available.

Table 7. Correlation coefficient (R^2) of glue factor and pressing time.

Birch and spruce	**Gas analysis method**	**Desiccator method**
Glue factor	0,2386	0,1991
Pressing time	0,3851	0,7385

Table 8. Correlation coefficient (R^2) of glue factor and pressing time (birch).

Birch	**Gas analysis method**	**Desiccator method**
Glue factor	0,0942	0,0270
Pressing time	0,0026	0,0795

Table 9. Correlation coefficient (R^2) of glue factor and pressing time (spruce).

Spruce	**Gas analysis method**	**Desiccator method**
Glue factor	0,0039	0,1042
Pressing time	0,0687	0,6833

As proven that neither the glue factor nor the pressing time has a predictable impact on the formaldehyde emissions, gives the opportunity to compare the test results as an average value. This also makes the outcome more trustworthy as there are more measuring points available to compare. Resin 1-3 represent plywood panels made out of birch while resin 4 and 5 are recipes for spruce panels. Resins 1, 2 and 4 are lignin-based resins. This information about resins is gathered in table 10 down below.

Table 10. Wood species and types of resin.

	Wood species	Resin type
Resin 1	Birch	LPF
Resin 2	Birch	LPF
Resin 3	Birch	PF
Resin 4	Spruce	LPF
Resin 5	Spruce	PF

As is seen from figures 10 and 11, spruce tends to have a higher level of emissions with both determination methods. With great expanded uncertainty of desiccator method, the FE of spruce panels might reach remarkably higher than the emissions of birch panels. The differences in emissions can be explained by the natural wood consistence of formaldehyde (table 3). This in turn confirms the assumption of the influence of wood species once again.

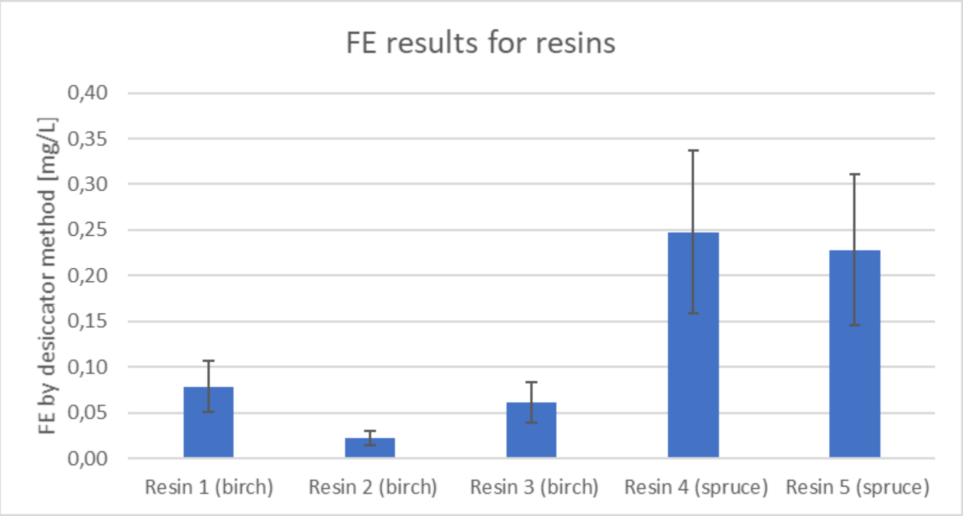


Figure 10. FE results for different resin types, desiccator method.

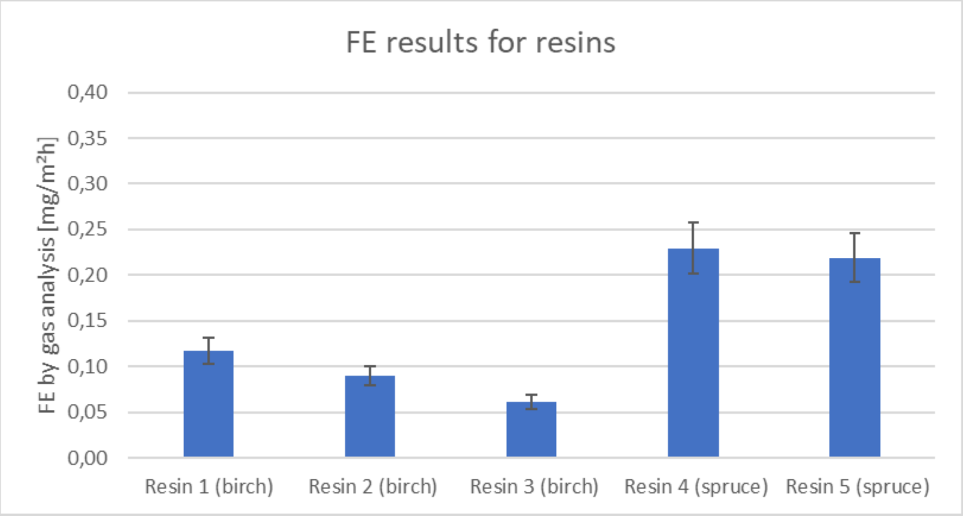


Figure 11. FE results for different resin types, gas analysis.

With smaller molar ratio, also the FE is estimated to be lower. The actual data for molar ratio is however not presented in this study, and the review concentrates on the relationship between FE and lignin. Focusing only on the birch panels, it is seen that resin 1 and 2 (which are lignin-based), do not differ considerably from resin 3 (which is phenol-based). In fact, with gas analysis method, PF resin actually has the lowest FE value of all the results. The same can be said with spruce panels. Resin 4 (lignin-based) really has a higher FE value than resin 5 (phenol-based) with both determination methods. It can be inferred that FE is independent from the amount of lignin in the resin.

7 CONCLUSIONS

One of the main targets of this thesis was to find a correlation coefficient for gas analysis and desiccator method. These methods measure the level of formaldehyde emissions from plywood panels. At this very moment, there is no EN-standard available for desiccator method. Strong correlation coefficient would give a possibility for utilizing this cost-efficient and accessible determination method in Europe. The emissions release could be measured close to the output of the panels and would also reduce the need for extra transport. This in turn would cut the GHG emissions.

Possible correlation coefficient would have assured the need and also the possibility of EN-standard for desiccator method. In this thesis, only the linear correlation was studied, and no clear correlation was found between these methods. It might be possible to find a correlation coefficient with a more complex equation, but this could be confirmed or repealed only with more research. Another major aspect affecting the current lack for EN-standard is the uncertainty of desiccator method. It was calculated that the expanded uncertainty of gas analysis is 12 % and the value of desiccator method is 36 %, which is remarkably higher compared to the gas analysis one. The lack of correlation and high uncertainty of desiccator method complicates the formation of reliable EN-standard.

Another main target of this bachelor’s thesis was the comparison of PF and LPF resin. In order to compare the formaldehyde emission levels of these resins, it was crucial to identify all the other variables affecting the overall emissions. Variables that were considered in this study were wood species, glue factor, pressing time, and resin type. Hypotheses for these variables affecting the FE (table 4) were collected from literature. Only the hypothesis for wood species was confirmed, and all the other variables did not appear to correlate with the emissions. The distinction between hardwood and softwood FE can be explained with the variation of natural consistence. Also, the recipes of the resins have differences and are estimated to have an impact on the release.

With superficial study of the lignin in the resin, no clear relationship between FE and lignin was found. The hypothesis of the study however concerned the molar ratio of the resin, not the actual amount of lignin. The recipes of resins could be studied more closely to achieve a better review of this relationship. Substitution of phenol still has big environmental impacts, even if the FE levels did not appear to decrease. By utilizing this renewable by-product for resin manufacturing instead for using it as a source of energy, less fossil raw materials are consumed. This in turn reduces the greenhouse gas emissions. GHG emissions can be reduced further by concentrating on the source of formaldehyde in resin. Instead of using traditional formaldehyde, it can also be produced from biomethane.

8 SUMMARY

The main targets of this bachelor's thesis were to study the correlation between gas analysis method and desiccator method and to compare LPF and PF formaldehyde emissions. The study was related to plywood manufacturing and was made in cooperation with UPM Biochemicals. The study is needed for predicting the results and for estimating the future actions for reducing the formaldehyde emissions.

In the literature part of the thesis, plywood manufacturing, components of the resin, and determination methods were studied more closely. Also, the standards and legislation related to plywood panels were observed. Hypothesis for the possible reduction of formaldehyde emissions with different parameters were made. The parameters studied in this thesis were wood species, glue factor, pressing time, and resin type. Error estimation for both methods were calculated.

In the result part of the thesis, all measurements were analyzed. Determination methods were compared to one another. The comparison led to a result of no clear correlation existing between gas analysis and desiccator method. Based on the research result, utilizing desiccator method with no EN-standard today is not possible. In the same chapter, hypothesis for different parameters affecting the FE were either confirmed or repealed based on test results. The effect of wood species was confirmed as it was detected that hardwood emits less formaldehyde than softwood. All the other hypotheses were repealed, as they were noticed not to have a clear impact on the FE of the panel.

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APPENDICES

Table 1. Description of the test pieces.

Adhesive	Structure	Glue factor [g/m^2]	Pressing time [min]	Formaldehyde emission	
				Des.	Gas
Resin 1	Birch 1,5 mm (9-ply, 12 mm)	145	8	0,090	0,123
	Birch 1,5 mm (9-ply, 12 mm)	163	8	0,150	0,148
	Birch 1,5 mm (9-ply, 12 mm)	154	8	0,140	0,089
	Birch 1,5 mm (9-ply, 12 mm)	145	9	0,030	0,094
	Birch 1,5 mm (9-ply, 12 mm)	154	9	0,020	0,124
	Birch 1,5 mm (9-ply, 12 mm)	163	9	0,040	0,124
Resin 2	Birch 1,5 mm (9-ply, 12 mm)	145	8	0,010	0,073
	Birch 1,5 mm (9-ply, 12 mm)	163	8	0,020	0,082
	Birch 1,5 mm (9-ply, 12 mm)	154	8	0,050	0,045
	Birch 1,5 mm (9-ply, 12 mm)	145	9	0,020	0,062
	Birch 1,5 mm (9-ply, 12 mm)	163	9	0,020	0,132
	Birch 1,5 mm (9-ply, 12 mm)	154	9	0,010	0,143
Resin 3	Birch 1,5 mm (9-ply, 12 mm)	154	8	0,030	0,090
	Birch 1,5 mm (9-ply, 12 mm)	145	8	0,030	0,062
	Birch 1,5 mm (9-ply, 12 mm)	163	8	0,070	0,108
	Birch 1,5 mm (9-ply, 12 mm)	154	9	0,080	0,072
	Birch 1,5 mm (9-ply, 12 mm)	163	9	0,070	0,015
	Birch 1,5 mm (9-ply, 12 mm)	145	9	0,090	0,021
Resin 4	Spruce 3,2 mm (5-ply, 15 mm)	128	6,5	0,380	0,179
	Spruce 3,2 mm (5-ply, 15 mm)	138	6,5	0,400	0,249
	Spruce 3,2 mm (5-ply, 15 mm)	148	6,5	0,340	0,221
	Spruce 3,2 mm (5-ply, 15 mm)	128	7,5	0,430	0,172
	Spruce 3,2 mm (5-ply, 15 mm)	138	7,5	0,390	0,249
	Spruce 3,2 mm (5-ply, 15 mm)	148	7,5	0,330	0,150
	Spruce 2,6 mm (7-ply, 18 mm)	118	8	0,110	0,104
	Spruce 2,6 mm (7-ply, 18 mm)	128	8	0,090	0,324
	Spruce 2,6 mm (7-ply, 18 mm)	138	8	0,120	0,290
	Spruce 2,6 mm (7-ply, 18 mm)	118	9	0,130	0,220
	Spruce 2,6 mm (7-ply, 18 mm)	128	9	0,140	0,242
	Spruce 2,6 mm (7-ply, 18 mm)	138	9	0,110	0,354
Resin 5	Spruce 2,6 mm (7-ply, 18 mm)	118	8	0,210	0,051
	Spruce 2,6 mm (7-ply, 18 mm)	128	8	0,210	0,118
	Spruce 2,6 mm (7-ply, 18 mm)	138	8	0,150	0,125
	Spruce 2,6 mm (7-ply, 18 mm)	118	9	0,170	0,288
	Spruce 2,6 mm (7-ply, 18 mm)	128	9	0,170	0,407
	Spruce 2,6 mm (7-ply, 18 mm)	138	9	0,160	0,293
	Spruce 3,2 mm (5-ply, 15 mm)	128	6,5	0,310	0,223
	Spruce 3,2 mm (5-ply, 15 mm)	138	6,5	0,230	0,198
	Spruce 3,2 mm (5-ply, 15 mm)	148	6,5	0,270	0,184
	Spruce 3,2 mm (5-ply, 15 mm)	128	7,5	0,310	0,334
	Spruce 3,2 mm (5-ply, 15 mm)	138	7,5	0,300	0,206
	Spruce 3,2 mm (5-ply, 15 mm)	148	7,5	0,250	0,202

APPENDIX II

Table 2. Uncertainty results of gas analysis method.

Measure 1	Measure 2	Average	d_i	d_{ri}(%)	$[d_{ri}(\%)]^2$
0,01975	0,01975	0,02	0,000	0,00	0,00
0,03175	0,03325	0,03	-0,002	-4,62	21,30
0,039	0,03975	0,04	-0,001	-1,90	3,63
0,0325	0,02125	0,03	0,011	41,86	1752,30
0,039	0,039	0,04	0,000	0,00	0,00
0,026	0,026	0,03	0,000	0,00	0,00
0,0165	0,0165	0,02	0,000	0,00	0,00
0,05775	0,05775	0,06	0,000	0,00	0,00
0,0525	0,05325	0,05	-0,001	-1,42	2,01
0,0465	0,04725	0,05	-0,001	-1,60	2,56
0,05025	0,0495	0,05	0,001	1,50	2,26
0,053	0,0525	0,05	0,001	0,95	0,90
0,003	0,0025	0,00	0,001	18,18	330,58
0,01975	0,01975	0,02	0,000	0,00	0,00
0,02	0,0205	0,02	-0,001	-2,47	6,10
0,00225	0,00225	0,00	0,000	0,00	0,00
0,021	0,0215	0,02	-0,001	-2,35	5,54
0,036	0,036	0,04	0,000	0,00	0,00
0,02475	0,02475	0,02	0,000	0,00	0,00
0,01275	0,01275	0,01	0,000	0,00	0,00
0,0105	0,0105	0,01	0,000	0,00	0,00
0,0505	0,0505	0,05	0,000	0,00	0,00
0,03025	0,02975	0,03	0,001	1,67	2,78
0,03675	0,03675	0,04	0,000	0,00	0,00
0,02175	0,02175	0,02	0,000	0,00	0,00
0,01575	0,01575	0,02	0,000	0,00	0,00
-0,0045	-0,005	0,00	0,001	-10,53	110,80
-0,004	-0,004	0,00	0,000	0,00	0,00
-0,00375	-0,0045	0,00	0,001	-18,18	330,58
-0,00375	-0,0045	0,00	0,001	-18,18	330,58
-0,0155	-0,015	-0,02	-0,001	3,28	10,75
-0,0135	-0,01275	-0,01	-0,001	5,71	32,65
-0,01675	-0,01675	-0,02	0,000	0,00	0,00
-0,014	-0,014	-0,01	0,000	0,00	0,00
0,022	0,02125	0,02	0,001	3,47	12,03
0,02325	0,024	0,02	-0,001	-3,17	10,08
-0,0125	-0,0125	-0,01	0,000	0,00	0,00
-0,017	-0,017075	-0,02	0,000	-0,44	0,19
0,0115	0,011	0,01	0,001	4,44	19,75
0,006	0,00525	0,01	0,001	13,33	177,78
0,003	0,003	0,00	0,000	0,00	0,00
0,00325	0,00325	0,00	0,000	0,00	0,00
				$\sum[d_{ri}(\%)]^2$	**3165,14**
Random error, S_{ri}(%)					**6,14**

Table 3. Uncertainty results of desiccator method.

Measure 1	**Measure 2**	**Average**	**d_i**	**d_{ri} (%)**	**$[d_{ri}$ (%)$]^2$**
0,363	0,375	0,37	-0,012	-3,25	10,58
0,368	0,393	0,38	-0,025	-6,57	43,17
0,323	0,326	0,32	-0,003	-0,92	0,85
0,41	0,397	0,40	0,013	3,22	10,38
0,371	0,38	0,38	-0,009	-2,40	5,74
0,3	0,335	0,32	-0,035	-11,02	121,52
0,114	0,096	0,11	0,018	17,14	293,88
0,086	0,094	0,09	-0,008	-8,89	79,01
0,102	0,135	0,12	-0,033	-27,85	775,52
0,142	0,138	0,14	0,004	2,86	8,16
0,145	0,145	0,15	0,000	0,00	0,00
0,116	0,093	0,10	0,023	22,01	484,42
0,205	0,247	0,23	-0,042	-18,58	345,37
0,229	0,201	0,22	0,028	13,02	169,61
0,18	0,148	0,16	0,032	19,51	380,73
0,171	0,173	0,17	-0,002	-1,16	1,35
0,169	0,16	0,16	0,009	5,47	29,93
0,158	0,162	0,16	-0,004	-2,50	6,25
0,308	0,305	0,31	0,003	0,98	0,96
0,223	0,214	0,22	0,009	4,12	16,97
0,279	0,233	0,26	0,046	17,97	322,88
0,282	0,303	0,29	-0,021	-7,18	51,55
0,28	0,294	0,29	-0,014	-4,88	23,80
0,247	0,233	0,24	0,014	5,83	34,03
0,109	0,09	0,10	0,019	19,10	364,64
0,134	0,18	0,16	-0,046	-29,30	858,45
0,162	0,113	0,14	0,049	35,64	1269,95
0,033	0,033	0,03	0,000	0,00	0,00
0,028	0,02	0,02	0,008	33,33	1111,11
0,034	0,036	0,04	-0,002	-5,71	32,65
0,01	0,013	0,01	-0,003	-26,09	680,53
0,016	0,015	0,02	0,001	6,45	41,62
0,044	0,062	0,05	-0,018	-33,96	1153,44
0,016	0,036	0,03	-0,020	-76,92	5917,16
0,022	0,02	0,02	0,002	9,52	90,70
0,013	0,007	0,01	0,006	60,00	3600,00
0,025	0,032	0,03	-0,007	-24,56	603,26
0,024	0,043	0,03	-0,019	-56,72	3216,75
0,058	0,093	0,08	-0,035	-46,36	2149,03
0,097	0,072	0,08	0,025	29,59	875,32
0,057	0,079	0,07	-0,022	-32,35	1046,71
0,098	0,082	0,09	0,016	17,78	316,05
				$\sum[d_{ri}(\%)]^2$	**26544,02**
Random error S_{ri}(%)					**17,78**

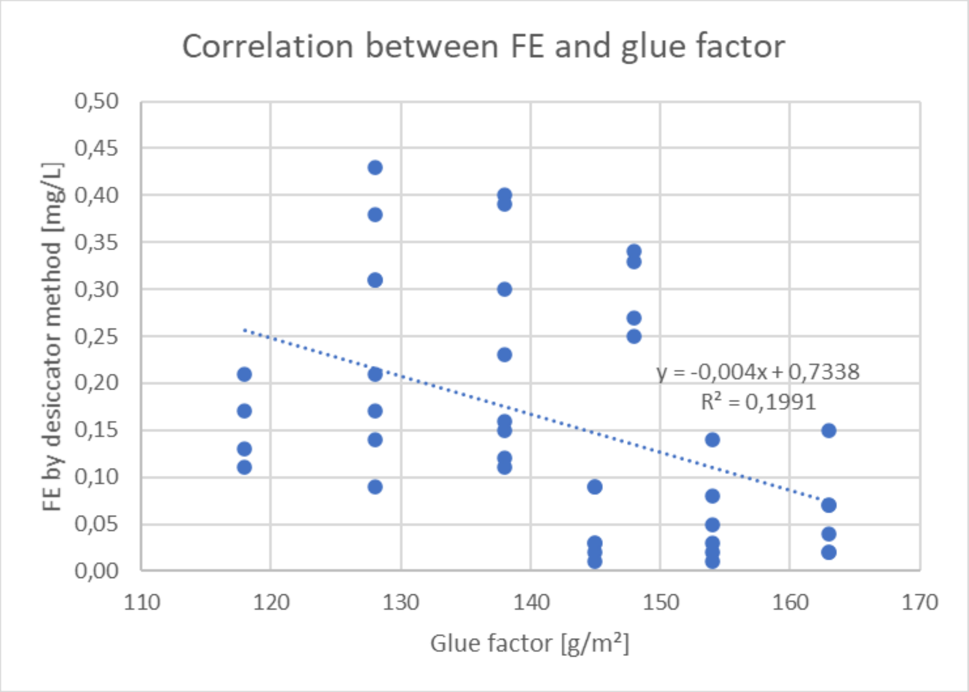

Figure 1. Correlation between FE and glue factor, desiccator method.

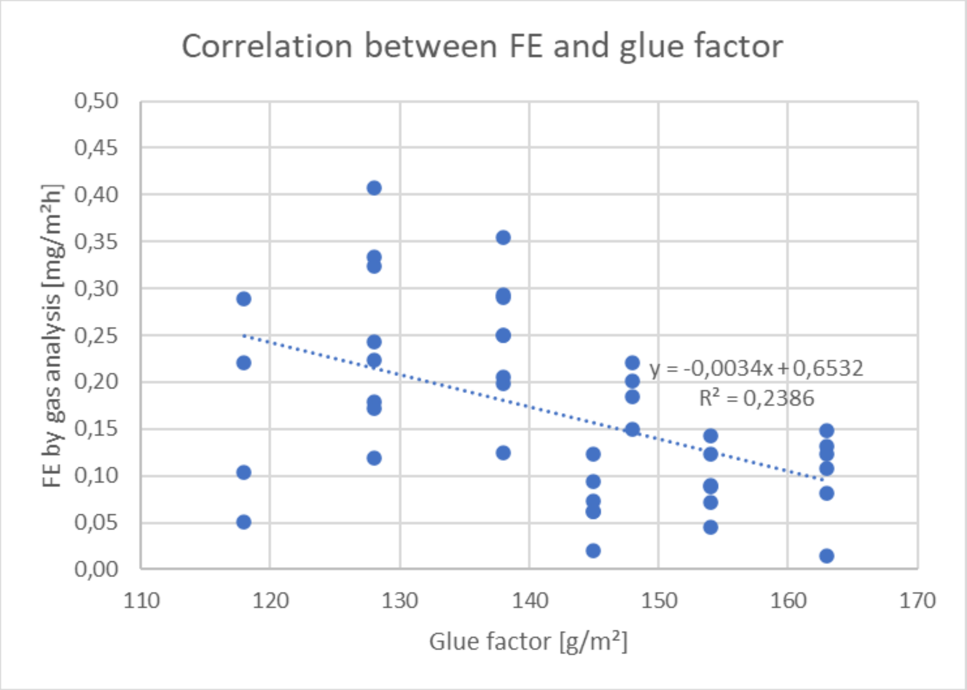

Figure 2. Correlation between FE and glue factor, gas analysis.

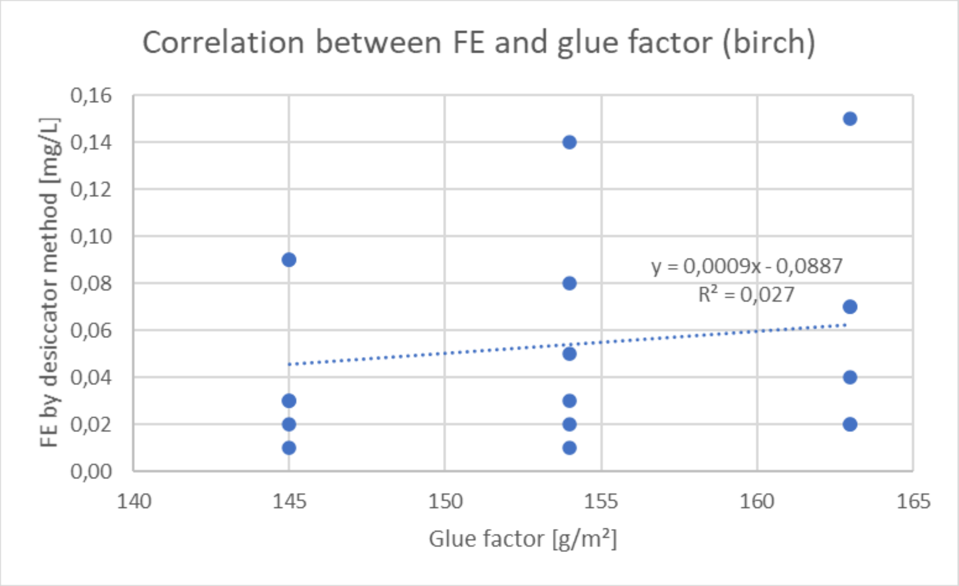

Figure 3. Correlation between FE and glue factor (birch), desiccator method.

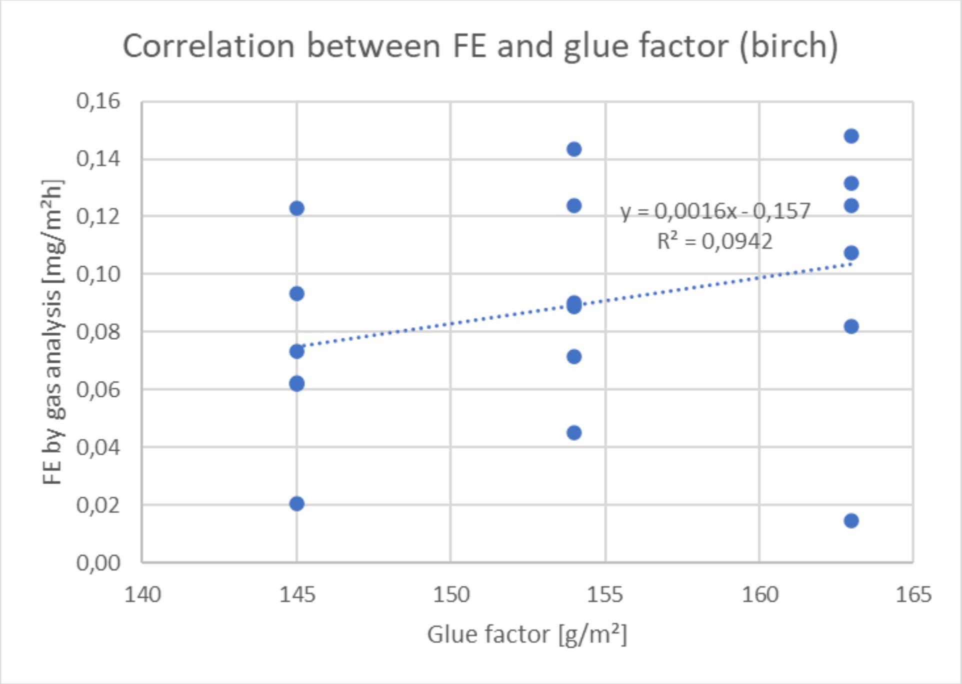

Figure 4. Correlation between FE and glue factor (birch), gas analysis.

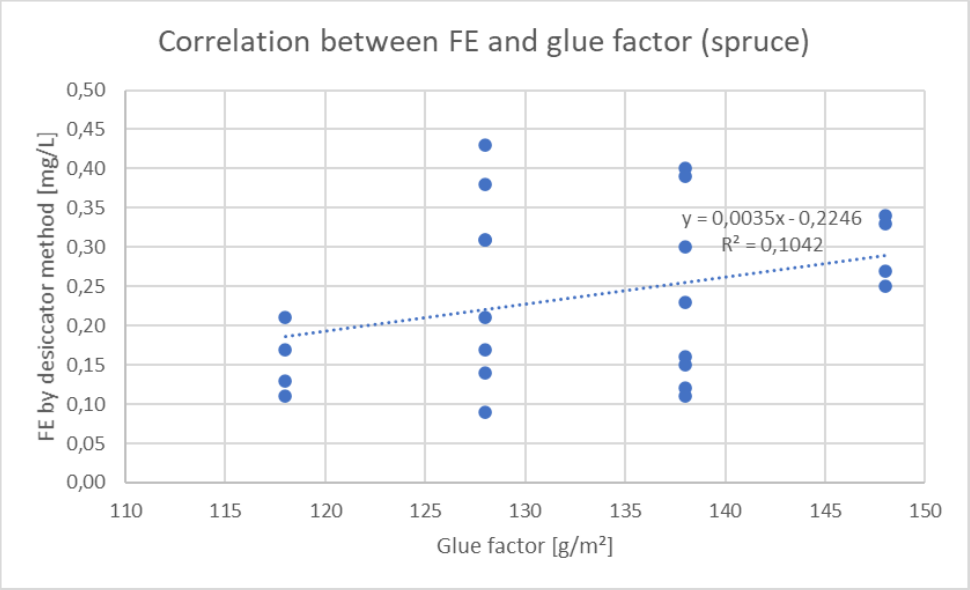

Figure 5. Correlation between FE and glue factor (spruce), desiccator method.

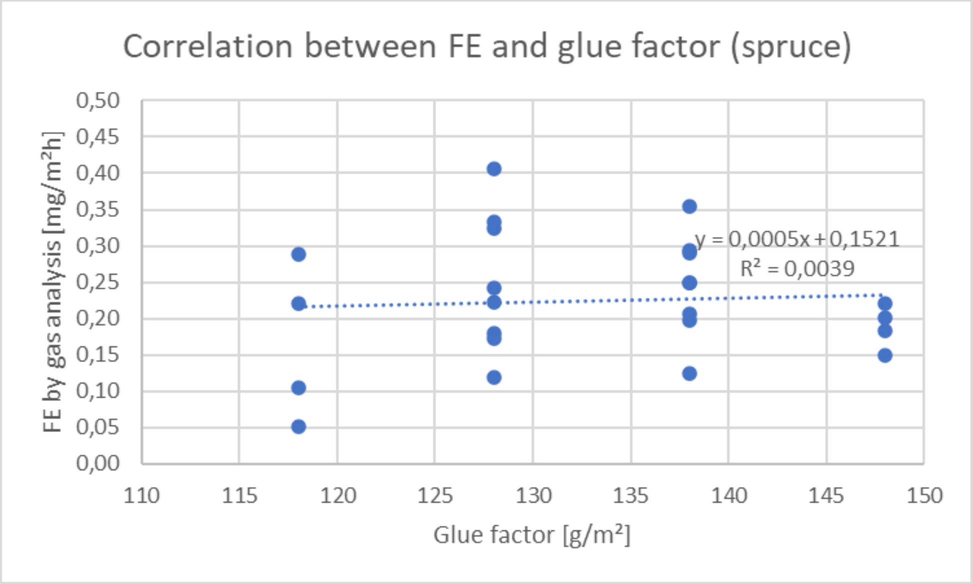

Figure 6. Correlation between FE and glue factor (spruce), gas analysis.

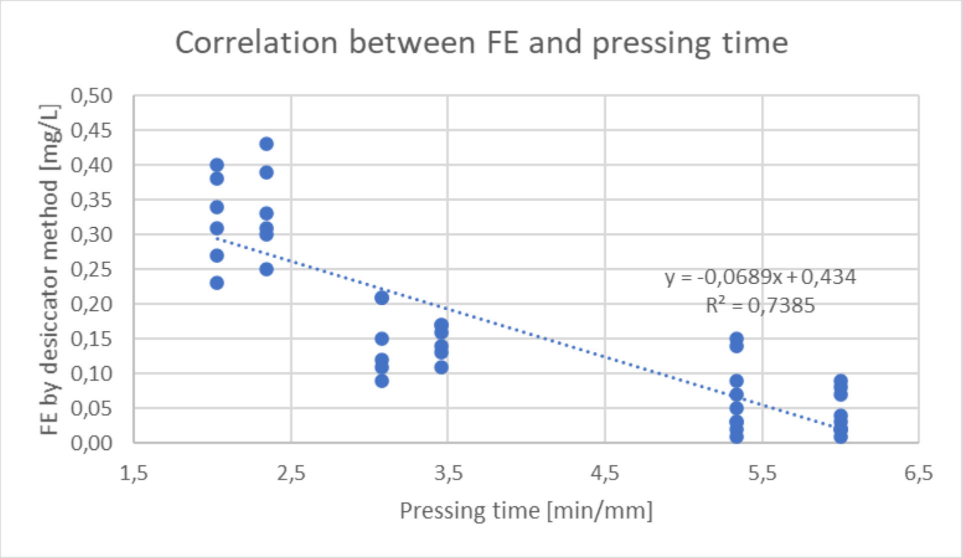

Figure 7. Correlation between FE and pressing time, desiccator method.

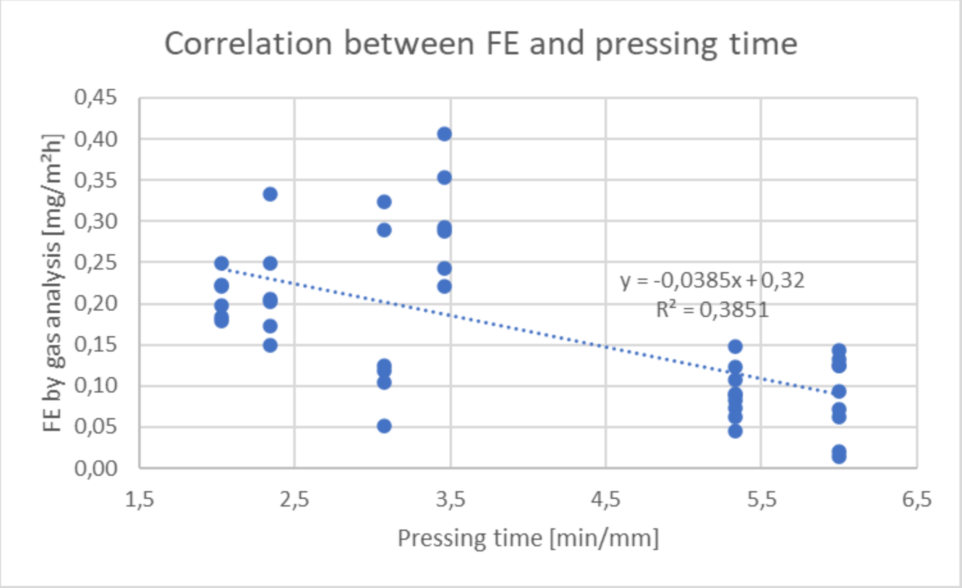

Figure 8. Correlation between FE and pressing time, gas analysis.

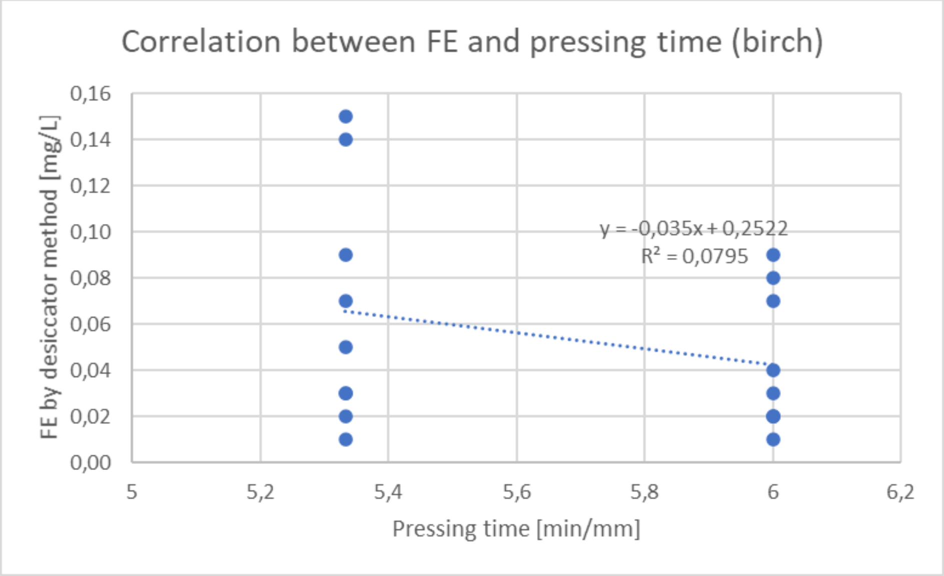

Figure 9. Correlation between FE and pressing time (birch), desiccator method.

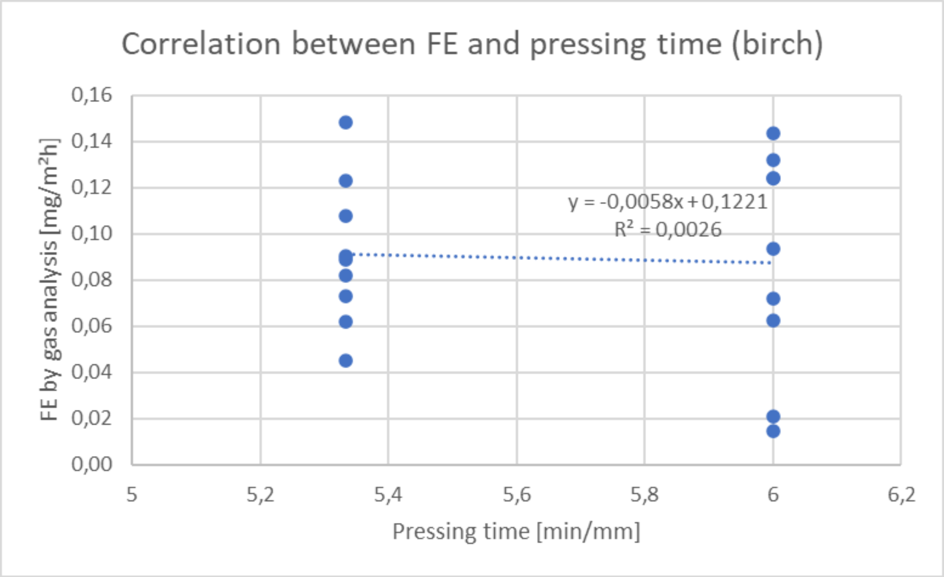

Figure 10. Correlation between FE and pressing time (birch), gas analysis.

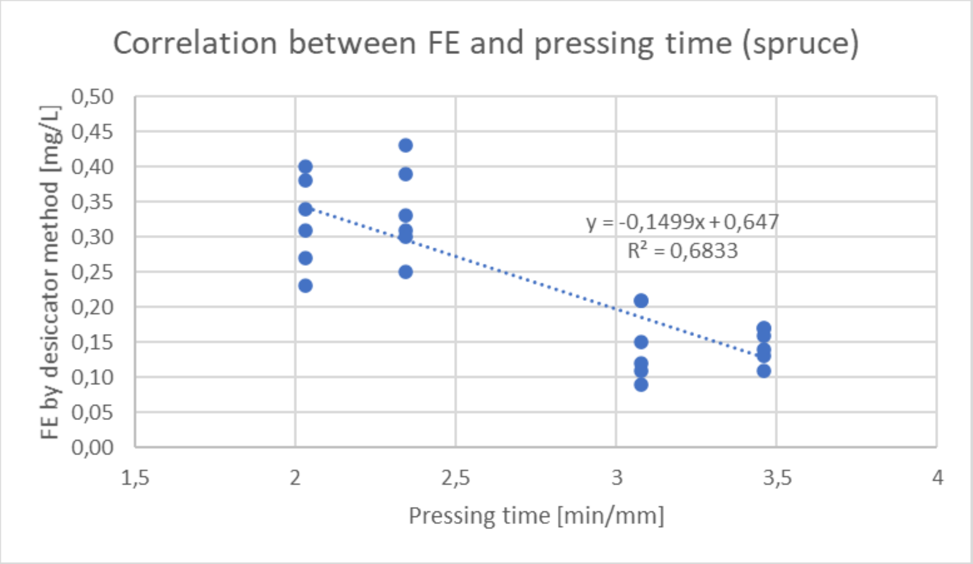

Figure 11. Correlation between FE and pressing time (spruce), desiccator method.

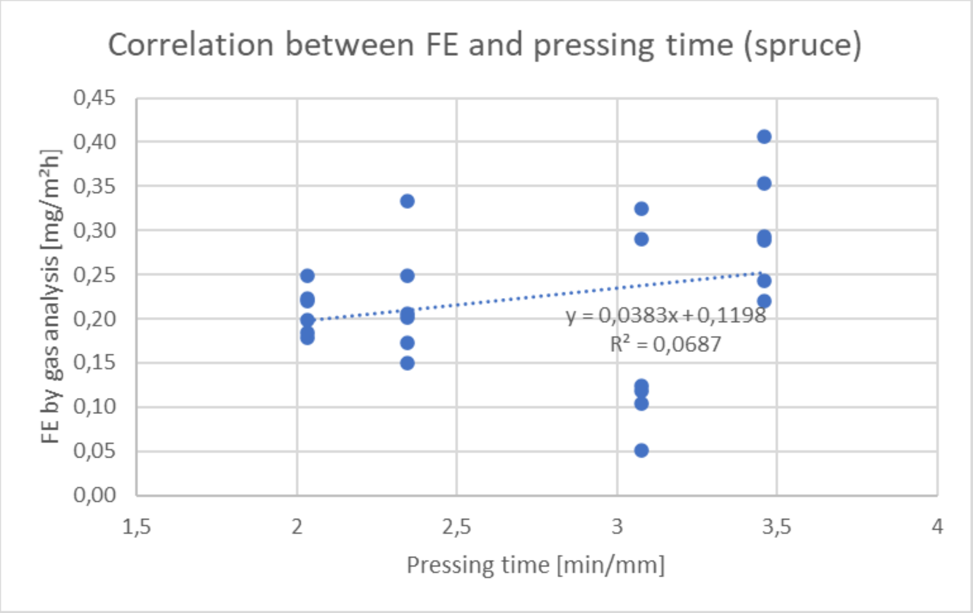

Figure 12. Correlation between FE and pressing time (spruce), gas analysis.