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FACULTY OF TECHNOLOGY

USING NIR TECHNOLOGY TO REDUCE THE NUMBER OF HAZARDOUS SAMPLES IN RESIN PRODUCTION

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DEGREE PROGRAMME IN PROCESS ENGINEERING
Master’s Thesis
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TIIVISTELMÄ OPINNÄYTETYÖSTÄ Oulun yliopisto Teknillinen tiedekunta

Koulutusohjelma (kandidaatintyö, diplomityö)
Prosessitekniikan maisteriohjelma

Pääaineopintojen ala (lisensiaatintyö)

Tekijä
Pikkarainen, Johan

Työn ohjaaja yliopistolla
Ahola J, TkT; Mikola M, FM

Työn nimi
Using NIR technology to reduce the number of hazardous samples in resin production

Opintosuunta	Työn laji	Aika	Sivumäärä
Kemiallinen prosessitekniikka	Diplomityö	Helmikuu 2021	75 s, 4 liitettä

Tiivistelmä

Diplomityön tavoitteena oli selvittää NIR teknologian potentiaalisuutta vähentää haitallisten näytteiden määrää sekä kartoittaa NIR teknologian käyttöä hartsituotannossa. Fenoliset hartsinäytteet ovat terveydelle haitallisia ja NIR on uusinta teknologiaa, jonka potentiaalisuutta tarkasteltiin diplomityössä. Työn kokeellisen osion tarkoituksena oli luoda NIR kalibraatiomallit erilaisille hartsimateriaaleille ja tutkia, kuinka luotettavasti NIR teknologialla voidaan analysoida ominaisuutta 1, hartsien ominaisuutta 2, ominaisuuksia 3 ja 4 hartsituotannossa.

Työn kokeellisessa osiossa kerättiin dataa hartsien loppunäytteistä tuotannon laboratoriossa käyttäen NIR anturia NIR spektrien luomiseen. Hartsit valmistettiin liimatehtaan panosreaktoreissa normaalin tuotannon yhteydessä ja datan keruu toteutettiin yhteistyössä tuotannon operaattoreiden kanssa. Referenssianalyysit suoritettiin datan keruun yhteydessä tuotannon operaattoreiden toimesta ja samalla luotiin referenssitulokset NIR:n antamille tuloksille.

Ominaisuuksien 1 ja 2 ennustamiseen löydettiin tarkat lähi-infrapunaspektroskopian aaltolukualueet, mutta ominaisuuksien 3 ja 4 ennustamiseen ei löydetty tarkkoja aaltolukualueita. NIR teknologia käyttää ominaisuuden 1 ennustamiseen aaltolukualuetta 6102-5446 cm^{-1} ja ominaisuuden 2 ennustamiseen aaltolukualuetta 6846-6900 cm^{-1}. Ominaisuuksien 3 ja 4 ennustamiseen käytettiin aaltolukualuetta 4000-12000 cm^{-1}, joka kattaa lähes koko lähi-infrapunaspektroskopian aaltolukualueen.

Tulosten perusteella NIR teknologia vaatii tarkat kalibraatiomallit hartsin jokaiselle analysoitavalle ominaisuudelle ja mallien luomista varten tulee kerätä arviolta 40-50 näytettä, jotta malleista saadaan riittävän tarkkoja ennustamaan referenssianalyysien tuloksia hartsituotannossa. NIR pystyy ennustamaan vähäiselläkin näytemäärällä referenssianalyysien tuloksia, mutta mallit eivät ole tilastollisesti merkittäviä normaalijakauman mukaisesti. Lineaarinen malli todettiin olevan paras malli ennustamaan referenssianalyysien tuloksia, mutta riittävän tarkkoja malleja ei saatu aikaiseksi diplomityön aikana. Tuloksia voidaan hyödyntää hartsituotannossa, sillä tuloksien mukaan haitallisten näytteiden määrää voidaan vähentää NIR teknologialla, jos malleista saadaan tilastollisesti riittävän tarkkoja ja kalibraatiomallien luominen opetusdatalla vaatii pitkäjänteisyyttä

Muita tietoja

ABSTRACT
FOR THESIS

University of Oulu Faculty of Technology

Degree Programme (Bachelor's Thesis, Master's Thesis) Master's Programme in Process Engineering	Major Subject (Licentiate Thesis)
Author Pikkarainen, Johan	Thesis Supervisor Ahola J, D.Sc. (Tech); Mikola M, M.Sc. (Tech)

Title of Thesis
Using NIR technology to reduce the number of hazardous samples in resin production

Major Subject	Type of Thesis	Submission Date	Number of Pages
Chemical process engineering	Master's Thesis	February 2021	75 p., 4 App.

Abstract

The goal of this master's thesis was to clarify the potential of the NIR technology to reduce the number of the hazardous samples and survey useful of the NIR technology in the resin production. The phenolic resin samples are toxic for the health and the NIR technology is the newest technology, whose potential was reviewed during the master's thesis. The purpose of the experimental section was to be created the NIR calibration models for each resin material and study how reliably the NIR technology can analyze the property 1, the property 2 for the resins, the properties 3 and 4 in the resin production.

During the experimental section was collected the data from final samples of the various resin materials using with the NIR probe in the manufacturing laboratory to be created the NIR spectra set. The resins were produced in the batch reactors in the resin plant and the data was arranged in the cooperation of the manufacturing operators. The reference analyzes were performed within the data collection in cooperation of the manufacturing operators and the reference results were created to be compared to the NIR results.

There was found the exact the wavenumbers of the near-infrared spectroscopy to be predicted the properties 1 and 2, but not was found the exact wavenumbers to be predicted the properties 3 and 4. NIR technology can be used to be predicted the property 1 using with the wavenumber of 6102-5446 cm^{-1} and the property 2 using with the wavenumber of 6846-6900 cm^{-1}. The wavenumber region of 4000-12000 cm^{-1} to be predicted the properties 3 and 4.

According to the results the NIR technology requiring the exact calibration models for each analyzable property of the resin and there is needed approximately 40-50 samples to be created models, which are enough precise to be predicted the results of the reference analyzes in the resin production. NIR is able to predict the results of the reference analyzes with the little sample set, but then the models are not the statistically significant. The linear model was noted to be the best model to predict the results of the reference analyzes, but the precise models were not achieved during the master's thesis process. The results can be utilized for the resin production and the hazardous samples can be reduced using with the NIR technology, if the models are the statistically precise and the creation of the calibration models need the patience.

Additional Information

PREFACE

The purpose of this master's thesis was to clarify the possibilities to use the NIR technology to reduce the hazardous samples in the resin production and the potential of the NIR device for the automation control system. The thesis resolved the possibilities to use the NIR technology to measure the properties of the many resins and the calibration methods for the resin production. The work took place from June 2020 to February 2021.

I would like to thank Petri Leskinen for giving me this opportunity and finding a challenge master's thesis subject at the end of process engineering studies. I thank my thesis supervisors Petri Leskinen (Hexion), Juha Ahola (University of Oulu) and Marja Mikola (University of Oulu) supervising me along this project with the instructions. Many thanks to Petri Päivinen, Sampo Hirvonen and Jani Toropainen for helping me by answering for many questions, giving the tips and collect data from the hazardous manual samples in the resin production.

Thanks to my parents and friends, who gave assistance for any issue. There have been many memorable moments during my chemical engineering studies and the long study time is coming to an end. The cure competence will come with time.

Kitee, 22.2.2021 Johan Pikkarainen

CONTENT OF TABLE

APPENDIXES:

ABBREVIATIONS

FIR	Far-Infrared
F/P	formaldehyde to phenol molar ratio
IR	infrared
NIR	Near Infrared
NIRS	Near Infrared Spectroscopy
MIR	Mid-Infrared
PF	Phenol Formaldehyde
PLSR	Partial least-squares regression
RMSE	Root Mean Squared Error
UF	Urea Formaldehyde
USDA	United States Department of Agriculture

MARKINGS

A	absorptivity
c	speed of light
c	concentration of molecules in beam
C_p	the ability index
C_{pk}	the ability index
E	photon energy
f	the number of oscillations
h	Planck's constant
l	thickness of centimeters of the measured sample at the specific concentration
I	detected energy after the interaction of the samples
I_o	the initial energy incident to the sample
k	absorption coefficient
r	correlation coefficient
R	reflected light
t	time period
T	transmittance

α	Alfa error is used in the comparative experiments
β	Beta error is used in the comparative experiments
λ	wavelength
ε	molar absorptivity
σ	sigma, the deviation of the process
ν	frequency

1 INTRODUCTION

An interest for the near-infrared spectroscopy (NIRS) has noted in the past years and this technique has potential to be used in the various analysis in the chemical industries. Benefits of NIRS are its the rapid, fast, and nondestructive analysis of the samples and the improvements in the instrumentation for the NIRS has influenced on the usefulness of the NIRS in the various industries. The major factor to use the NIRS is its ability to solve analytic analysis fast and quickly. (Siesler *et al*. 2002, p. 11)

The high demand for the product quality management in the chemical, petrochemical, polymer, pharmaceutical and food industries have influenced on the specific and more environmentally friendly analytic tools. Vibrational spectroscopy techniques such as the mid-infrared, the near infrared and the Raman have taken place in the quality control and the process monitoring in the last years. Vibrational technique the NIRS has taken a giant leap as the analytical tool in the various industries. (Siesler *et al*. 2002, p. 1)

The near infrared (NIR) technology has been reported to be used in the various industries such as in the agricultural, polymer, petroleum, and fuel industries successfully. The NIR technology can be used for the quality control in the automation system and it offers fast response for in-line application. In fact, development of the NIRS was done by the agricultural area and this field area launched the NIR technology. The development work of the agricultural area influenced on the NIR technology progress and it has reached applicability in many industry areas nowadays. (Pasquini 2003, p. 214)

According to Finnish safety and the chemical administration the plants should maintain and expand the safety actions, the hazards for health, environment, and assets in the plant actions, and consider the operating conditions and the safety level (TUKES 2020a). *The hazardous samples* cause harm for health and environment. Reducing the hazardous samples, the safety level can be maintained in the chemical industry plants and the operators have ability to work more safety without the hazardous samples. This is responsible safety and healthy work.

The hazardous samples such as the phenolic and the aldehydic samples cause risks for the employees’ health and the hazardous samples have the remarkable impact for environment at Hexion in Puhos industrial area. In addition, the 2 of the products the takes too much time to analyze at this moment and this analysis of the 2 could be done with the NIRS device. The operators of resin plant would be able to see straight the 2 and they are able to control the production processes, if the NIRS device has implemented to the control system. The implementation of the NIRS devices to the control system would increase the quality of resin products and productivity, decrease the defects of the batches and the operators could focus to control the resin processes at Hexion.

This master thesis is done for Hexion Kitee site, which is in Puhos industrial area near Kitee, in South Karelia in Finland. Puhos industrial area are included Hexion Oy, Surfactor Finland Oy, and Stora Enso Wood products Oyj. Maintenance companies Caverion Oy and Seppo Eskelinen Oy are also part of Puhos industrial area. Hexion Kitee site produces formaldehyde at concentration of 52 %, resins and hardeners. The phenol and amino resins are used in plywood, automotive, coatings, composites, and abrasives applications. Hexion deliveries resins and hardeners for Finland, Russian and other countries. The resins production has started in 1972 at Puhos site. Puhos industrial area can be seen in the figure 1. (Hexion 2019b; Kitee 2020)

Figure 1. Puhos industrial area, Hexion Kitee site is in the middle. (Hexion 2019a)

Hexion Kitee site plant has 2 amino resins manufacturing batch reactors, 3 phenolic resins manufacturing batch reactors, 2 specialties and additives pilot reactors and 2 additives manufacturing batch reactors. Furthermore, Hexion Kitee site has boiler house, that produces 13 GWh in yearly. It uses the light fuel oil, the liquefied petroleum gas, and the tail gas to create energy in the boiler. The tail gas is fed to the boiler from sidestream of the formalin plant.

This master thesis will introduce the resin production, the near-infrared spectroscopy technology, and the NIR technology in the online analysis tasks. The mechanism of the NIRS will be introduced to clarify for the analysis of phenolic and aldehyde samples, to measure 2 of the products and the 4 in the literature section. The NIRS device is implemented to the batch reactors and the results is analyzed with Minitab in the experimental section.

Goals of this master thesis are to reduce the hazardous hand samples and resolve the potential of the NIRS device for the automation control system. It needs to find out the possibilities to use the NIRS devices for analysis tasks at Hexion. The experimental tests are arranged to find out the correlation with the hand taken samples for the analyses. The following questions are tried to reply in this master thesis process:

- How reliably the properties of 1, 3, 2 in the products and 4 can be analyzed using with NIR technology?
- Is there possibility to reduce the hazardous samples using with NIR technology at Hexion Kitee site?
- Which of the hazardous samples can be reduced using with NIR technology?
- How accurately the properties, phenolic and aldehyde samples, the 2 of the products, 3 and 4 can be measured using with NIR technology?

The analyzed results will be represented based on the literature and the experimental section and the proposed actions are given. In addition, the further research and development topics are raised in the conclusion chapter.

2 RESINS PRODUCTION

This chapter will introduce the commercial production of formaldehyde as the continuous process and resins production as the batch processes. The primary function of the Hexion Kitee site is to produces formaldehyde, the numerous resins and energy by the boiler house in Kitee. Hexion Kitee produces phenol-formaldehyde resins, urea-formaldehyde resins, and the powder hardeners.

2.1 Formaldehyde plant

Formalin is aqueous solution of formaldehyde which is produced by oxidation of methanol and it is the applicable raw material in the production of urea, melamine and acetal resins, and plastic products nowadays. In fact, the German professor Hoffmann prepared formaldehyde first time in 1867 and soon Hoffmann's method was approved in commercial formaldehyde production. Because of Hoffmann's method formaldehyde can be produced in a continuous process in the commercial scale. The production of formaldehyde has increased significant at the beginning of 1940 century, formaldehyde is produced 25-27 million tons in yearly worldwide and the formaldehyde continuous process has important impact in chemical industry on today. (Hader *et al.* 1952, p.1; Qian *et al.* 2002, p. 1)

Formaldehyde has ability to react with both organic and inorganic compounds. This allow formaldehyde to be used in many application areas and the consumption of formaldehyde has raised since the first world war. In fact, about 55 % of total formaldehyde production based on the silver catalysis reaction in 2000 and the advantages of the process are the low investment cost, the high yield, and the stable production all the time. (Hader *et al.* 1952; Qian *et al.* 2002)

The first commercial production process of formaldehyde was stated in 1901 in the United States. The production process was based on German process and it used a copper catalyst. Later, a silver catalyst was used to produce more formaldehyde with higher yields. It is known, that yields of formaldehyde are 85-90 %, but the higher yields are possible to achieve with special forms of silver. (Hader *et al.* 1952, p. 2)

The over 90 years old commercial production process is still in use in the Hexion Kitee site and the continuous formaldehyde plant produces formaldehyde of concentration of 52 %. Methanol and oxygen are fed continuously to the vaporizer and further to the catalysis reactors. The catalyzed reactors with silver catalyst produce formaldehyde gas. The formaldehyde plant including a vaporizer, 2 heterogeneously catalysis reactors and an absorber tower. The vaporizer, the silver catalyst reactors and the absorber tower are presented in the following sections with the illustrative figures.

Vaporizer

The function of the vaporizer is to vaporize the methanol-water-mixture in the closed vessel, in which the process conditions are pressure of 0.12 bar and temperature of 65-70 °C. Methanol, water and oxygen are fed continuously to the vaporizer to be formed the gas mixture of the methanol and water. The mixture of methanol-water is fed to the vaporizer at the concentration of 28-30 % methanol and this concentration is controlled by the methanol addition. The formed gas mixture is fed to the heterogeneously catalysis reactors.

Silver catalysis reactors

The silver catalysis reactors are used to produce the formaldehyde and the chemical reactions are heterogeneously catalyzed by the silver crystals. The process conditions are temperature of 600 Celsius degree (°C) and pressure of 0.11 bar. The vaporizer mixture of the methanol and water is passed through the 2 parallel reactors to form formaldehyde gas.

The formaldehyde gas is formed by the heterogeneously catalysis reactions and the main principal reactions are (1) and (2), which are presented below. The first reaction (1) was approved since the 1950s in the production of formaldehyde and the reactants of methanol and oxygen are reacted to formaldehyde gas in the excess air in the catalyst bed. Second, the reaction (2) was accepted in the 20th century and the reaction forms formaldehyde gas and hydrogen. Overall, the reactions are the parallel reactions, and the reaction (1) is preferred to produce the formaldehyde gas and the reaction (2) is the secondary in the production of the formaldehyde gas. (Hader *et al.* 1952, p. 3; Qian *et al.* 2002, p. 1)

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O \qquad \Delta H = -159 \text{ kJ/mol} \qquad (1)$$

$$2\ CH_3OH \rightarrow CH_2O + 2\ H_2 \qquad \Delta H = +84 \text{ kJ/mol} \qquad (2)$$

The silver catalysis reactors consist of the catalyst tubesheet, the heat exchanger and the reaction bed. The methanol-water-mixture is fed to the top of the silver catalyst reactor, the reactants are reacted in the middle of the reactor and the product gas is moved off from the bottom of the reactor.

Absorber Tower

The formed gas mixture of the formaldehyde and methanol gas from the silver catalysis reactors is fed to the absorber tower to separate the desired formaldehyde. The formaldehyde plan therefore consists of 1 separation unit and it enables the rich product of formaldehyde. The formaldehyde is absorbed to the water to be formed the aqueous solution of formaldehyde and the aqueous solution is often called for formalin. The absorber tower is the last process stage of the formaldehyde plant.

To sum up the production process there are some sensitive operating parameters, which influencing to the reactions from the methanol to formaldehyde. Such as the reaction temperature, residence time and the molar ratio of H_2O/CH_3OH, which can be manipulated to get the maximum production of formaldehyde in the production scale. The yield of formaldehyde increases with temperature and it achieves the maximum in the temperature of 923 K and above this temperature the formaldehyde decomposes to hydrogen. The residence time is also influence to the conversion and selectivity to formaldehyde, methanol, and hydrogen.

2.2 Resin plant

Hexion Kitee site consists of the resin plant and its function is to produce the amino resins, the phenolic resins, the urea resins, the melamine resins, the specialties, and the additives. The resins are used in many applications, such as for the coatings, the plywood and the automotive (Hexion 2019b; Jin *et al.* 2015, p. 1). The resins are produced by the batch reactors with the cooling and the heating jacket, and the charging pipelines to feed many raw chemicals, such as the acids, the bases, and many other chemicals. The figure 2 describes the batch reactor, in which many resins are produced in Kitee. The cooking times vary from the 5 hours to 12 hours.

Figure 2. Batch reactor to produce various resins in Hexion Kitee.

Phenolic resins are produced by condensation polymerization utilizing the reaction of formaldehyde with phenol. Resins type is based on the catalyst and molar ratio of phenol to formaldehyde. The base catalyst resulting the resole types and the molar ratio of phenol to formaldehyde is over 1 in the production of the resoles. The resoles are the aqueous solution of the formaldehyde and phenol in physically, the stability is quite limited, and their functional groups are methylal and phenolic. (Gardziella *et al.* 2000, p. 25)

There are many reaction stages to produce the resins in the manufacturing batch reactors. The reaction synthesis of the resins is a very complicated, there are several reaction paths and it is an exothermic synthesis; therefore, the process control and monitoring are the critical factors to successfully produce the resins. The synthesis of the resins consists of the following stages and these are presented in the figure 3. (Monni 2008, p. 8)

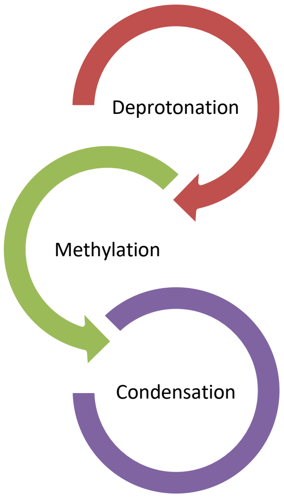


Figure 3. Main stages of resin synthesis and its proceedings.

The deprotonation, methylation, condensation is proceeded a row, or they take place as parallel and these reaction stages are to be specified the properties of resins. The phenol and formaldehyde are used to produce the resins as the main raw materials and the caustic is used as the homogeneously catalyst to be catalyzed the synthesis of the resins. (Monni 2008, p. 8)

The function of the deprotonation is to remove a proton from a caustic and therefore the phenol and the caustic react in the deprotonation stage. After the deprotonation stage the phenol and formaldehyde react in the alkaline media to form a phenoxide ion and further the formed the phenoxide reacts with formaldehyde to produce the hydroxymethylphenol. The reaction of the methylation stage is a highly exothermic and the function of the methylation stage is to consume the phenol and the formaldehyde prior to the condensation stage.

Finally, the condensation stage takes place, and the polymers of the resins are formed in the reactions of the phenolic species in the synthesis of the resin. The condensation reactions involving the reactions of the methylol groups and to be formed methylene and ether links between the hydroxymethylphenols. (Monni 2008, p. 8-10)

3 NEAR INFRARED SPECTROSCOPY

The history of the NIR analysis has many approaches and all approaches have influenced to these days. The main scientist for the NIR analysis has been the astronomer William Herschel at the beginning of 19th century. According to the historical development (Burns & Ciurczak 1992, p. 1) Herschel discovered the white light with a thermometer and a glass prism, and Herschel succeeded to be separated the colors of the white light. As the result of his discoveries the red spectrum was found, and Herschel named it for the infrared (IR).

Many years later an IR spectrometer was built by W.W. Coblentz and the measurements were done at each wavelength to analyze samples. Soon, there was found that no two compounds have the same spectra and therefore the IR spectrum is a key to identify each compound. In fact, wavelength region between 2 and 15 μm is called for the fingerprint region. The first the IR instruments was available at the middle of 19th century and the instrument recorded the spectra within 15 minutes. (Burns & Ciurczak 1992, p. 2)

The NIR instrumentation was added to the practical application in the 1940s and the modern NIR analysis was invented by USDA (United States Department of Agriculture) in 1950s. Thanks to Karl Norris this NIR analysis was developed, and it enable to control the agricultural commodities rapidly. In fact, USDA found the NIR of non-destructive reflectance and it enabled the huge rise to use the NIR technology in the field of agricultural. Furthermore, the development of NIR analysis by USDA has influenced in many fields of chemical industry, such as petrochemical, pulp and paper, and pharmaceutical industry to be implemented the NIR technology. (Rantanen 2000, p. 3)

Today, the NIRS has the useful applications and the excellent approval for the qualitative and the quantitative analysis in the food, the chemical and the oil industry. The advantages of the NIRS are its speed in the analysis tasks, the low cost, and the non-destructive influence. The IR instruments can record the spectra under 1 minute and the performance of IR instrument have improved within the hundred years (Burns & Ciurczak 1992, p. 2). The improvement of the NIRS instrument has influenced its interest in the analysis tasks and the fibre optics development has improved its performance. (Roggo *et al.* 2007, p.1)

3.1 Physical foundations

This subchapter will go through the electromagnetic waves, the photon energy, and the electromagnetic spectrum. All of these linked to the infrared spectroscopy and the theoretical background will be given.

The electromagnetic waves are the critical factors for the any material at the various frequencies and therefore are the main statements in the NIRS technology. The quantum physics states that the electromagnetic waves are packets of energy and these packed energies call for the photons. As more the higher frequencies, the photons have more energy to influence for the molecules and the electrons to be vibrated. (Schmitt 2002, p. 1)

The physical foundations clarify the electromagnetic spectrum has the exact wavelength, the time period and the quantum of energy. These definitions are presented with the following equations (3), (4) and (5) below.

Wavelength, λ, which is the distance between peaks of a wave.

$$\lambda = \frac{c}{f} \tag{3}$$

where
λ is the wavelength
c is the speed of light
f is the number of oscillations.

Time period, t, which is the time between peaks of a wave

$$t = \frac{1}{f} \tag{4}$$

where
T is time period
f is the number of oscillations.

Photon energy, which is the minimum value of energy that can be transferred at this frequency

$$E = hf \tag{5}$$

where
f is the number of oscillations per second
c is the speed of light
h is Planck's constant.

As more the photon has energy, then the more intensity of the photon can affect to the molecules. As shorter the wavelength is then more intensity the infrared wavelength has. The wavelengths for each IR radiation zones are represented as the nanometers in the table 1. The range of the NIRS spectral is around 800-2500 nm in wavelength and it covers from the visible spectral range to the mid-infrared region. Furthermore, the IR has the ranges of the mid and the far infrared spectral regions, respectively. The mid infrared spectroscopy (MIRS) covers spectral range around 2500-25000 nm as the wavelength and the far infrared spectroscopy (FIRS) covers spectral range around 25000-1000000 nm as the wavelength. (Roggo *et al.* 2007, p. 2; Rantanen 2000, p. 3)

Table 1. The infrared radiation zones and their wavelength ranges as the nanometers.

IR radiation zone	Wavelength range in nm
NIR	800-2500
MIR	2500-25000
FIR	25000-1000000

3.2 Grounds of the near infrared spectroscopy

The subchapter of the molecular spectroscopy theory is dealt with the vibrational motions, the changes of the energy levels in the molecules, the spectra response for the concentration and the absorptivity of the molecules.

The molecules can vibrate, wag, bend or rotate and this feature is utilized to read the spectra. In fact, the spectra are the result of the vibrational motions, such like the motions of the vibrate, wag, bend or rotate. Every single motion vibrating at the exact wavelength in the region of the NIR and the studied details have publicly available. The aqueous solution of every single can be measured with the spectroscopy technologies. (Workman & Weyer 2008)

Any energy of the rotational, vibrational, and electronic motion is influenced to the spectra, whereas the translational energy is not influenced to the spectra. First of all, the rotational energy is directly proportional to the velocity of rotation and therefore the molecules have more rotational energy as more the molecules rotate. Second, the electronic energy can be described with Pauli principle and the quantum numbers. Third, the vibrational energy is influenced more to the spectra as the other motions and therefore the vibrational motions have the major influence on the characteristic of the spectra. (Workman & Weyer 2008)

The molecules have the three degrees of freedom for the vibrational motions and there are three dimensional directions (x, y, z), as well. Also, there are three rotation motions to be considered. However, the linear molecules have 3N-6 motion types and each motion has the specific frequency to vibrate by IR radiation. The vibrational motions can be considered as harmonic if the bonds do not break and the bonds are to be stretched approximately 10-15 %. (Workman & Weyer 2008)

Due to absorptivity there has assumed that a change in the spectral response is directly proportional to a concentration (Workman & Weyer 2008, p. 2). This supposition can be described by the Bouguer, Lambert and Beer relationship or Beer’s law. The Beer’s law is described in the quotation marks below.

> *''The absorbance (A, AU, or signal strength) of an analyte being measured using a spectrophotometer is equivalent to the product of the absorptivity (e) of specific type of molecular vibration; the concentration (ε) of the molecules in the measurement beam; and the pathlength of the sample holder within the measurement beam.'' (Workman & Weyer 2008, p. 2)*

However, the direct relationship from the spectral signal to the concentration can be presented as the following equation (6).

$$\mathrm{A} = \ \mathrm{\varepsilon cl} \tag{6}$$

where
A means absorptivity
ε is the molar absorptivity in units of dm mol^{-1} cm^{-1},
c is the concentration of molecules in the spectrometer beam in units of mol dm^{-1}
l is the thickness in units of centimeters of the measured sample at a specific concentration.

Transmittance (T = 0.0-1.0) or percent transmittance (T = 0-100.0) spectroscopy can be presented with the following terms and equations (7).

$$\mathrm{T} = \frac{\mathrm{I}}{\mathrm{I_0}} = 10^{-\mathrm{\varepsilon cl}} > \mathrm{Abs.} = \mathrm{A} = -\log_{10}\left(\frac{\mathrm{I}}{\mathrm{I_0}}\right) = -\log_{10}\mathrm{T} = \mathrm{\varepsilon cl} \tag{7}$$

where
I is the detected energy after the interaction of the samples and I_0 means the initial energy incident to the sample.

Today, many spectrophotometers use this assumption to measure the data as transmittance (T) or reflectance (R).

3.3 Vibration motions

The IR radiation has the electromagnetic spectrum from 800 nm to 1 mm and this range is involved the numerous vibrational modes. All these regions have the overtones and the combination bands, which are to be vibrated at the various frequencies. The overtones are linked to the bands, that are the step transition, and the combination bands are linked the combination of two independent molecular vibrations. The NIRS utilizes these bands to analyze the food, polymer, and agricultural products to be obtained the qualitative and the quantitative information from the samples. (Cozzolino 2013, p.18)

The incident light gives the molecules to vibrate and it is provided the fingerprint region to identify the any unknow molecules and the molecular species (Cozzolino 2013, 18). The beam of light is caused the vibrational stage in the various molecules and the vibrations is utilized in the any IR technologies. The vibrations of the stretching and bending are to be presented in the following subchapter to demonstrate their function in the IR technologies.

3.3.1 Stretching vibrations

The desired molecules can be vibrated as the symmetric or the asymmetric stretching and the vibrations are represented in the figure 4 using with the molecule of the formaldehyde below. The molecules (1) and (2) illustrate the asymmetric stretching and the molecule 3 illustrate the symmetric stretching in the figure 4. In fact, the stretching vibrations need the molecules to have three atoms in order that the stretching vibration would be possible to achieve (Workman & Weyer 2008, p. 3).

However, for the first instance of the stretching (1) the oxygen is moving away and the hydrogen atoms are approaching each others in the asymmetric stretching, whereas (2) the the oxygen atom and the hydrogen atoms moving away at the same time in the symmetric stretching. There also difference between these vibrations, that the asymmetric stretch is vibrated at the higher frequencies as the symmetric stretch.

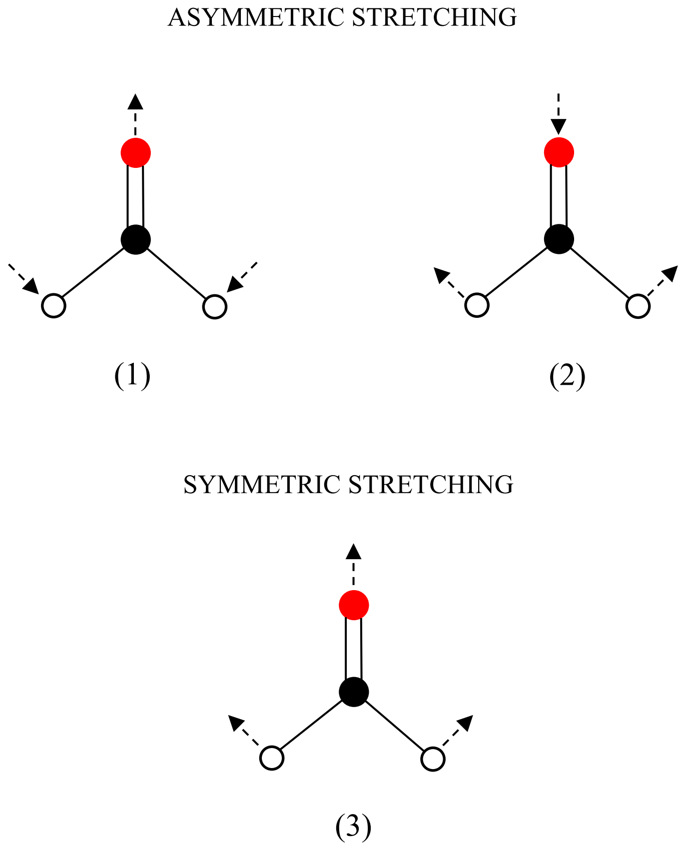


Figure 4. The illustrative demonstration of the symmetric and asymmetric stretching. (Retelled Workman & Weyer 2008, p. 3-4)

3.3.2 Bending vibrations

For the vibration motions are involved also the other motion group and these are called for the bending vibrations. In fact, the bending vibrations are to be vibrated at the lower frequencies as the stretching vibrations and the bending vibrations differ from each other by the bending forces in the atoms and by the bending movements. The bending vibrations occur, if the molecules at least four atoms and the molecules are to be vibrated as the symmetrically or symmetrically.

The figure 5 illustrates the bending vibrations and the types of the motions. The vibrations of the symmetric bending (1)(2) give to the bonds of the molecules to be moved for the other directions, whereas the vibrations of the asymmetric bending (3)(4) give the bonds of the molecules to be moved for the same directions. (Workman & Weyer 2008, p. 5-6)

SYMMETRICAL BENDING

ASYMMETRICAL BENDING

Figure 5. The illustrative demonstration of the symmetrical and the asymmetrical bending vibrations. (Retelled Workman & Weyer 2008, p. 6)

3.4 Overtone absorptions, peaks, and positions

This subchapter is looked over the NIR spectra of the overtone and the combination bands, the frequencies, and the intensities of the NIR spectra, and the function of the functional groups in the NIR spectroscopy.

The NIR spectra of the overtones and the combination bands are the main regions to investigate the NIR spectra. The absorption bands of the functional groups have listed in the table 2. Around the regions of the NIR spectra the NIR incident radiation gives to the vibrations for the functional groups and therefore the key elements are the frequency and intensity of the NIR spectra. In fact, the functional groups can vibrate and that can be identified from the NIR spectra. Identification of the NIR spectra and the analytical proceed are the remarkable steps to get some information from the samples. (Siesler *et al.* 2008, p. 33)

Table 2. The absorption bands of the functional groups and their region of the wavenumber.

Absorption band	Wavenumber, cm^{-1}
First overtone	7000-5000
Second overtone	10000-6000
Third overtone	14000-9000
Combination	5200-4000

Every functional group has the own overtone and the combination bands. In fact, the strongest absorptivity responses are obtained in the first overtone and the absorptivity response weaken to moving the second and third overtones. However, the absorptivity response is strong in the combination band, but many functional groups can vibrate in the combination band. (Conzen 2014, p. 39-55)

The covalent bonds of compounds can vibrate at the high energy levels cause the high amplitude and intensity for the NIR spectra. The NIR spectra is made by the absorptions, such as some functional groups. The desired functional groups are able absorb the NIR radiation at the overtones of stretching bands or the combinations of the stretching and bending bands. (Siesler *et al.* 2008, p. 33)

The region of the NIR spectra consists of overtones and the combinations of stretching and bending vibrations from the 800 nm to 2500 nm (Burns & Ciurczak 1992, p. 566). From the appendix 2 can be seen the overtone regions and their places in the NIR spectra. There are available 3 the overtone regions and 1 the combination region in the NIR region, each region of the functional groups can vibrate. Furthermore, the functional groups and their vibrational wavelengths are listed in the appendix 1. The appendix 1 shows the wavelengths (nm) or the wavenumbers (cm^{-1}), in which the functional groups can vibrate. The typical functional groups are that containing C, H, O, N, S or P atoms, and their functional groups are the methyl, the alkenes, the alcohols, the carboxylic acids, the aldehydes, and the aromatic groups.

The resins or the organic polymers are composed by the carbon, hydrogen, and nitrogen atoms, therefore the NIR spectra of the resins can be obtained from the specific functional groups (Burns & Ciurczak 1992, p. 566). This shows that the NIR spectroscopy is the excellent tool the measure the concentrations of resin products or the properties of resins by utilizing the specific functional groups in the aqueous solution of the samples and the intensities from the NIR spectra.

3.5 NIR spectra

This subchapter is looked over the properties of the resins, such as the 3, the 2 content, the aqueous concentration of formaldehyde and phenol and the 4. The goal of this master's thesis to investigate the correlation from the NIR spectra to the analyzed results of the resins.

The great advantage of NIR spectroscopy is that both physical and chemical properties of the samples can be measured at the same time and anyone physical separation or dissolution no needed. Using with NIR spectroscopy there is the easy sample handling, and the nondestructive analysis is possible. It has mentioned that Log 1/R spectra can be correlated to the numerous physical properties of the samples. (Burns & Ciurczak 1992, p. 569)

3.5.1 Functional groups as the characteristics of the resins

The functional groups are the key elements to identify many characteristics and properties of the resins at the region of the NIR. Utilizing the functional groups, the several properties of the resins can be solved out using with the NIRS. The functional groups and their ability to vibrate at the exact wavelengths and wavenumbers have been listed in the appendix 1.

However, there are 4 bands, such as the 3 overtones and the combination bands in the region of the NIR spectra. Each band can be utilized to resolve any property of the resins. The 3 and the concentration of the phenol can be resolved from the functional group of the aromatic, the concentration of the formaldehyde from the functional group of the aldehyde and the 2 from the water molecules. In fact, the functional groups acting like keys to resolve any property of the resins and the exact group need to be selected, if wanted to resolve the properties.

The correct absorptivity bands are able to correlate for the exact concentration of any components and these correct absorptivity bands defining the accuracy and usability of the NIR calibration model. Therefore, the interpretation of the NIR spectra is the major matter for the successfully usage of the NIRS. (Conzen 2014, p. 53-55)

3.5.2 Intensity peaks of the NIR spectra

The intensity of the spectra reveals the quantities of the concentrations and the intensities are the keys to establish the concentrations from any solutions. The usable absorptivity band is defined in the intensity of the absorbance response in the NIR spectra. The NIRS is used the absorptivity responses from 0.7 to 1.0 in each absorptivity band. The absorptivity response below 2.5 shall be used for the analysis, if there are not the suitable absorption bands in the NIR spectra. However, the absorptivity responses over 2.5 should not be used for establishing the concentrations from the samples. (Conzen 2014, p. 40)

NIR spectroscopic has 2 unique performance indicators to be indicated its performance, the detection limit and sensitivity (signal-to-noise). In fact, the detection limit can be owned for any NIRS technology or application, and these have equal to three times the SEC (standard error of calibration) and therefore there are two sample with various concentration. Further, the sensitivity of NIR spectra for any NIR method is meant the signal-to noise or the ratio of peak height for any compound at the specific wavelength. The sensitivity can be also described as the slope of the calibration line, in which are compared the concentration (y axis) to the optical response (x axis). (Burns & Ciurczak 1992, p. 250-251)

4 NIR TECHNOLOGY

The optical spectrometers, such as the Raman, the mid-infrared and the NIRS devices are used for the online process monitoring and the optimization nowadays. NIR spectroscopy allows to use the large sample volume/thickness, the light-fiber optics and there is possibility to separate the spectrometer device from the sampling points, such as the reactors and the pipelines. NIR is non-destructive technology and it enables to measure the organic compounds without the pretreatment. The analyzable samples can be either the solids, the liquids or the gas, and there is no need the weighting, the dilution or react to the chemicals. (Siesler *et al.* 2008, p. 9; Larkin 2011, p. 1)

The strengths of the NIR spectroscopy are the process monitoring without delay time, the short measuring time (15 seconds) and the use of NIR spectroscopy in all process conditions. The NIR device is suitable for the process monitoring as the on-line or the in-line method. In fact, the chemical and the physical properties can be defined from the samples just 1 NIR measurement. The advantages of the NIR spectroscopy are the considerable compared to the wet chemistry of the analytical methods. (Bruker 2020a; Larkin 2011, p.1)

However, there are the constraints for the NIR spectroscopy. The NIR technology is not suitable for the non-organic samples and neither for the samples with low concentrations. There are also some differences for measuring the aqueous solutions, which need to be considered using with NIR spectroscopy. The NIRS needs the high wavelength reproducibility, so that a standard deviation 0.02 nm will achieve. In fact, an acceptable tolerance is (+-) 5 nm and the calibrations are needed to ensure the wavelength differences. The corrections must make if the wavelength differences are not within a standard of 0.02 nm. (Marten *et al.* 1989, p.12; Siesler *et al.* 2008, p. 9-10; Larkin 2011, p. 1)

The NIR technology has been developed many years and it has potential for the chemical industry to be the tool for the quality control and monitoring today. This technology is provided the high-quality results and leading to a better understanding and control of the processes. Just compared to other optical spectroscopy technologies NIR technology is the best alternative for the industrial scale at this moment. (Siesler *et al.* 2008, p. 10)

4.1 NIR matrix F

Hexion Kitee is used the NIR matrix F device to measure the samples from the reactors and pipelines. The MATRIX-F FT-NIR device has many key advantages, such as the high accuracy of the in-line method, the optional built-in 6-port multiplexer, the direct method transfer, the low maintenance design, the matrix is available for the Ex hazardous areas and the ethernet connectivity is possibly. The NIR matrix F is presented in figure 6. The NIR matrix, the fibers, and the transmission probe can be seen in the figure 6.

Figure 6. The NIR matrix F and its instrumented devices. (Bruker 2020a)

The MATRIX-F has 6 internal multiplexed to allowing to connect the fiber-coupled from the matrix to the probe. The NIR matrix is also robustness, the long-term stable and it is easy to maintenance. Thanks to the fiber optic technology the MATRIX-F device can be placed hundred meters away from the actual measuring point. In fact, the performance can be optimized by utilizing the fiber optic technology and the extreme conditions shall be eliminated by using with the fiber optic technology.

4.2 Immersion probes

Immersion probes are used for FT-NIR measurement in the process control and the immersion probes have varietal material available. The reactors and the pipelines have equipped with standard connection ports for the immersion probes and therefore the installation is very easy. The immersion probes can be divided to three groups, which have listed below.

- Transmission Probes for clear liquids
- Reflection Probes for solid materials
- Transfection Probes for suspensions or emulsions

The transmission probes use the mono fiber, the transflectance and reflectance probes use the fiber bundles. For the probes have available the various types of the fiber optic cable and the fiber optic cables are produced with the exact path length. The types of the immersion probes are presented in figure 7. Each probe has been designed to measure the specific samples and in the process conditions. The transmission probes can be used for the clear liquids, the reflection probes for the solid materials and the transfection prober for suspensions or emulsions.

Figure 7. Types of the immersion probes. (Bruker 2020b)

4.3 Principle of near-infrared spectroscopy

Instrument of NIR technology can be divided to 4 class depending on the principle of the NIRS. The instruments have been designed to optimize for the specific purpose of the sampling, or to be solved the variate measurement problematic in manufacturing areas (Burns & Ciurczak 1992, p. 39). In fact, the NIR instruments can be categorized with their optical configurations, the scan rates, the source type, the detector type, the vibration-tolerant or the optimized design. The NIR instrument can be designed for the near-infrared transmittance (NIT), the near-infrared reflectance (NIR) or the reflectance and/or transmittance (NIR/NIT). (Burns & Ciurczak 1992, p. 39-40)

The NIRS is based on measuring the absorption and emission of the organic compounds by the feeding the infrared radiation to the samples. This leads to the vibrations in the covalent bonds of the dipole molecules. Each of the NIRS principle has been designed on the specific material and purpose. (Rees 2010, p. 2)

Regardless on principle of the NIRS, the incident light is mainly going through the sample and causing vibration motions in the samples. From the sample comes whether reflection, photoluminescence, transmission, or scattering light depending the principle of the NIRS (Van Suijlekom 2020). The figure 8 illustrates the various principles of the NIRS.

TRANSMISSION TRANSFLECTION

REFLECTION INTERACTION

Figure 8. Sample interactions of NIRS in the various principles and techniques. (Retelled Siesler *et al.* 2002, p. 119)

First, the method of the transmission NIRS is measured the number of the absorbed NIR radiation from the samples at the various wavelengths. This method is suitable for the aqueous samples, which are able to be transmitted IR radiation thought the samples. Second, the method of the reflection NIRS is measured the number of the reflected NIR radiation from the samples. This method is used for the solid materials. Third, the method of the transflection NIR is applied for the samples with the low concentrations. The NIR radiation is passed through the samples many times and leads to the higher absorptivity in the NIR spectra.

The NIR spectrometer does not need the high demand power and the measurement is done under the challenge conditions. The data is collected from the production reactors or pipelines, which are the difficult conditions to collect the data. To be compared to other IR spectroscopy technologies, the NIR spectrometers do not need so much power as the visible or the UV spectroscopy. The samples are often rough and heterogeneous, which are measured by the NIR spectroscopic. (Siesler *et al.* 2002, p. 43)

4.4 NIR calibration model

One step to implement the NIR technology is creating the NIR calibration model by the statistical program and its function is to relate the collected samples to the NIR spectra data. The calibration is needed to ensure that the NIR model is accuracy to interpret any concentration of the sample. Multicomponent solutions are quite complex and therefore the minor changes in absorbance means the concentration changes of the samples, the concentrations shall be varied from exact values and differences are depend on varietal applications. (Burns & Ciurczak 1992, p. 247)

In practical, NIRS calibration is involved to populate the samples set from the manufacturing site, measuring NIR spectra for entire sample set and performing the wet chemical analysis for all samples. The calibration model is needed to compute to calibrate or validate the measured sample set. In fact, the calibration is done for the renewed sample, whereas the validation is done for the known samples in manufacturing. However, the validation testing is performed always for the NIR calibration model and thereafter the routine analysis is performed in the manufacturing. The NIRS calibration process flow is illustrated in the figure 9.

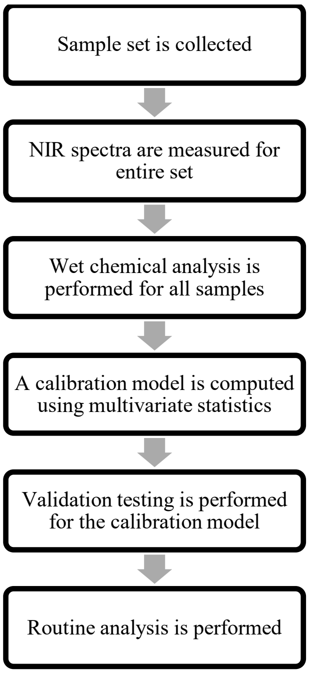


Figure 9. NIRS calibration process flow and process steps to illustrative the implementation of NIR.

Still, the NIRS calibration process needs the regular sample check and the validation for the NIR calibration model. If the sample set is not accurately analyzed by NIRS, there are causative agents such as the instrument failure or the wet chemistry analytics. However, NIRS technology is involved many approaches, such as analytical chemistry, statistic and NIRS programmer (Burns & Ciurczak 1992, p. 250). To real world involved instrument noise, nonlinearity between NIR data and analyzed concentrations, scattering, errors in reference results, physical variations in samples and unstable samples, and sampling errors (Burns & Ciurczak 1992, p. 252).

However, the empirical calibration methods are needed to use NIR in practical. The calibration equations based on the multivariate techniques to be accounted any variety from the real processes (Burns & Ciurczak 1992, p. 253). All these need to manage using NIRS technology successfully in the manufacturing areas.

4.4.1 Multivariate calibration method

Multivariate calibration plays the statement to record the quantitative information from multivariate data and to be created the multivariate calibration model to establish many variables from measured referenced values. (Martens 1985, p. 8)

Calibration model is the main tool to predict the concentrations of the any components and therefore the calibration model needs to create with the NIR technology. As an ideal case, Beer's law can be applied to simplify the calibration model, in which has only one component and the usable spectrometer has not noise available or any failures possibility. In this ideal case, the spectrum shall be shown as linear line. In fact, the absorbance peaks are directly proportional to the concentration of any components and then calibration model can be easily determined by the two samples and using with common mathematical formulas. (Burns & Ciurczak 1992, p. 107)

The ideal calibration model is determined by plotting the sample set and the straight line can be drawn for all data. Further, the unknown sample can be determined by measuring the absorbance at the absorbance axis and then projecting to the concentration axis reading the predicted concentration. (Burns & Ciurczak 1992, p. 109)

4.4.2 Partial least-squares regression (PLSR)

Multivariate data analytical technique relates to the partial least-squares regression (PLSR) designing the calibration model using with the NIR technology. In fact, PLSR is based on Herman Wold's principle and PLSR is capable to solve the multivariate analysis problems by the simple least-squares regressions. First, this PLSR method is presented as two-block regression method and it has been applied to NIR data by Martens and Jensen. (Burns & Ciurczak 1992, p. 159)

Main purpose of this PLSR is to predict the concentrations from the optical densities at the various wavelengths with the presented predictor equation (8) as shown. If sample set of the calibration is collected, then parameters in this equation can be estimated statistically. All of these obtained, so this predictor equation can be used to converting X data into estimates y in the following sample sets. Furthermore, PLSR method is a bilinear method, which collects a minor number of factors and PLSR method use the collected factor for y. Then, the abnormal NIR spectra of the calibration sample set can be detected. (Burns & Ciurczak 1992, p. 159)

$$y_i = b_o + \sum_{k=1}^{K} x_{ik} b_k \tag{8}$$

where y_i is concentrations in objects i = 1, 2,…, x_{ik} is a set of optical densities at wavelengths k = 1, 2,…K

PLS regression

Estimation of the model for y variable can be proceed, so that factors a = 1, 2,…, A are estimated and eliminated at each time. Each factor scores estimated after previous a-1 factors given the following equation (9).

$$t_a = E_{a-1} w_a \tag{9}$$

Further, the loading weight spectrum $W_a = (w_{ak}, k = 1, 2, \ldots, K)^T$ is defined as covariance matrix between the centered y variable and the residual variability remaining the previous a-1 factors (Burns & Ciurczak 1992, p. 166)

Calibration

Multivariate calibration of PLSR include on the model parameters, such as the optical number of factors to mode and each factor is estimated at a time prior to the next factor to be estimated. The calibration model include on parameters, such as $\bar{x}$, $\bar{y}$, A, $\widehat{W}$, $\hat{P}$, $\hat{q}$, and many statistics based on $\hat{T}$, $\hat{E}_A$ and f_A to scores $\hat{t}_a$ and any residuals. All these parameters are useful for reading the calibration data from NIR and to detect any outliners. (Burns & Ciurczak 1992, p. 167)

Once the calibration model has estimated, then the model can be used for predicting the samples of the concentrations from the optical densities. Each new sample with the input data scoring t_{ia} by the following equation (10).

$$t_{ia} = e_{i,a-1}^{T} w_a \tag{10}$$

where $e_{i,a-1} = x_i^T - \bar{x} - \sum_{m=1}^{a-1} \hat{t}_{im} \hat{p}^T$

and further y_i is predicted with the following equation (11)

where $$\hat{y}_i = \bar{y} + \sum_{m=1}^{a-1} t_{im} \hat{q}_m \tag{11}$$

Validation

After calibration its need to decide the optimal number of PLS factors and finalize the calibration model for NIR. There are should be only the predictive factor in the calibration model, so that it is ability to predict the concentrations of the samples. In fact, few factors cannot to create good model for NIR, whereas too many factors arise noise into the calibration model. Cross-validation is a tool to finish the calibration model in way, that each time a new sample set is cross-validated. To be finished the calibration model the estimated predictive errors were tested with the root mean square error of prediction (RMSEP) and the optimal number of factors is determined, if RMSEP is not decrease anymore. Moreover, the predictive PLS regression has been very successful for the multivariate calibration. (Burns & Ciurczak 1992, p. 167-168)

4.5 Statistics regression

To be entered the calibration model into practical it needs many programs calculations to fit the calibration model to the data and capable to predict the properties of the hazardous samples. Such as methods are p-value concerning the normal probability distribution, coefficient of determination (R^2), the multiple correlation coefficient (r), RMSE (Root Mean Squared Error) and the any residuals. (Burns & Ciurczak 1992, p. 118)

Statistics methods are critical to fit the calibration model into practical and manage the data collection, using the statistical methods and fit the model to the data, then the calibration model has possibilities to the predict any properties of the samples. Nowadays, many statistical methods are proceeded by the statistical programs.

Linear regression is the method to evaluate the performance of the models. Its need to determine the correlation coefficients for the models and fitting the model to data using with the partial least-squares regression. The general progress of the regression analysis is the following procedure. (Sorsa 2018, p. 15)

1. Choosing the model structure
2. Identification of model parameters
3. Evaluation of the model in statistically
4. Changing the model, if needed

There are the teaching, validation and testing data to be used in the statistic regression procedure. The teaching data is used to identification of the models, the validation data is used to validate the model structure and the test data is used to test the general performance of the models. All data has its own function to fitting the model to data. In fact, the data can be distributed or used the leave-one-out (LOO), K-fold or leave-multiple-out (LMO) methods. (Sorsa 2018)

Goodness of the model can be tested with ANOVA procedure and testing the significance of the regression coefficients using with t- or F test. Accuracy of the model can be evaluated with the correlation between the measured and the predicted values, squared R R^2 and the mutual information. These evaluations are performed for the NIR models and the equations of the linear correlation (12) and the squared R (13) are following. (Sorsa 2018)

Linear correlation

$$r_{xy} = \frac{1}{(n-1)s_x s_y} \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) \tag{12}$$

where r_{xy} is the linear correlation between the actual and predicted values

n is the number of the samples

Coefficient of determination (R^2)

$$SS_M = \sum_{i=1}^{N}(\hat{y}_i - \bar{y})^2 \qquad SS_E = \sum_{i=1}^{N}(\hat{y}_i - y_i)^2 \qquad SS_T = \sum_{i=1}^{N}(y_i - \bar{y})^2$$

$$R^2 = 1 - \frac{SS_E}{SS_T} \tag{13}$$

where SS_M is the medium sum of square

SS_P is the predicted sum of square

SS_R is the real sum of square

R^2 is the coefficient of determination to prove the goodness of model

Modeling error can be evaluated with the RMSE (14) (Root Mean Squared Error) and the relative error. These indicators are given information about modelling errors and the equations are presented.

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\hat{y}_i - y_i)^2} \tag{14}$$

where n is the number of the samples

$\hat{y}$ is the predicted value

y_i is the actual value

Residuals are errors for the tolerance of the predicted values from the actual values. The NIR models are good, if the residuals are normal probability distributed and extraordinary. The normal probability of the residuals can be tested with Kolmogorov-Smirnov method or using with the normal probability plot to be evaluating their normal probability. In fact, the residuals are given information about property of the model structure and which model structure would be correct.

5 PURPOSE AND GOAL

Main subjects of this master thesis are the hazardous samples and the manual sampling problematic by the operators in the resin manufacturing in Kitee. The hazardous samples are collected from the batch processes in the production of resins and the huge part of producing products including the hazardous samples, which are taken manually by the operators. In practical, every resin product has numerous hazardous samples, which should be reduced to the lower number and further improve the operators' work by considering the safety and health issues. Furthermore, to be reduced the hazardous samples the operators can be worked in a more safety and healthy in the resin plant. In addition, implementing NIR technology to Hexion Kitee site the quality of resins products can be improved, because the analysis tasks are completed by the NIR-device, not by the operators. In fact, it has been noted, that the samples can be analyzed in the different ways and the results can be varied by the operators. NIR technology improves the operational reliability and the processes capability, and the detects of the products can be reduced in the long term.

The hazardous manual sampling and the health hazards are the business metrics. The safety is the critical to the operators and the hazardous manual sampling by the operators is the main subject. This problem first was observed in January 2019 and the problem will be solved during this master thesis process. The materials with zero hazardous manual sampling will not be considered and only the materials with the numerous hazardous manual sampling will be considered in this master thesis. The output of results is represented with analysis results, which are collected during the experimental sections.

Purpose of experimental section is to collect NIR spectra from the hazardous manufacturing samples and understand the functionality of the NIR spectroscopy in the manufacturing environment. Furthermore, there is a need to understand numerous variation sources influencing to the NIR spectra have regarding measuring the NIR spectra from the hazardous samples. The measurements are performed with the NIR matrix F and the transmission probes, which one has implemented to the manufacturing reactors area and another has in the manufacturing laboratory near the control room. Regarding the NIR measurements the OPUS program is utilized to store all NIR spectra files.

Goal is to collect the large sample set for the analysis section and prepare to create the NIR calibration model further investigations. The NIR spectra is measuring from the hazardous samples, which are going to collect the hand samples and straightly from the manufacturing reactors without pretreatment. The measurements are performed at the temperature of 25 °C and the analysis of the wet chemistry are including to the experimental section, as well. The properties 3, 2, 4 and 1 and formaldehyde are performed by the operators or laboratory technicians. All results from the wet chemistry analyzes are collected to the list further investigations and any concerns or observations are recording to analyze the functionality of the NIR spectroscopic measuring in the manufacturing area.

5.1 Number of hazardous manual samples in 2019

Hazardous manual samples contain the phenol, which has not been reacted in the batch reactors. The total number of hazardous manual samples was counted during summer 2020 in Kitee. The aqueous concentration of phenol and the total samples for each material were considered in the calculations, and the total manual samples were calculated finally. Total number of hazardous manual samples was taken precisely 4697 times by the operators in 2019. The number of the hazardous manual samples was calculated from the folders of the production recipe during the master thesis process in summer 2020. The taken samples were the in-process samples.

The determined materials were allocated to three categories and there are following ranges. Materials, which have the aqueous concentration of phenol over 5 %, 1-5 % and phenol under 1 %. The hazardous materials can be managed a better way and focus on the most hazardous materials in the experimental section. The most hazardous materials have been listed in the figure 10 and the aqueous concentration of phenol in the final samples. The survey work shows that the most hazardous materials are C, O and B, which contain the aqueous concentration of phenol over 8 % and the mentioned materials are very toxic for the operators. Hexion Kitee manufacturing 9 materials including the aqueous concentration of phenol over 5 %, 5 materials have phenol 1-5 % and 30 materials have phenol under 1 %.

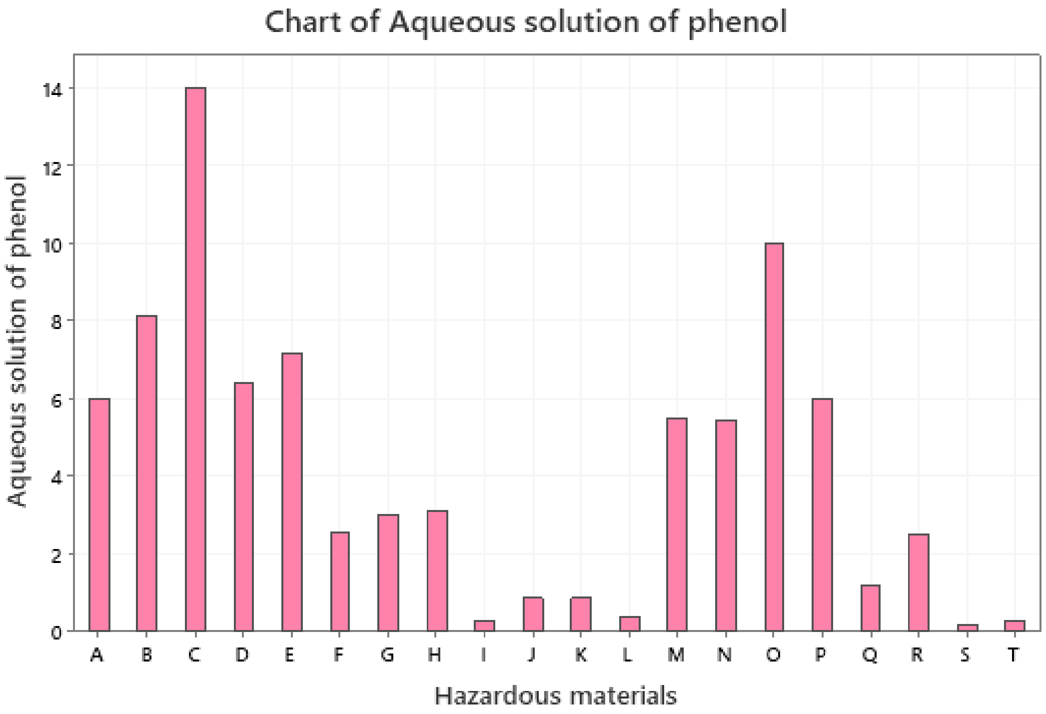


Figure 10. The values for the aqueous solution of phenol in the hazardous materials.

The manual samples were taken the most during the batch production of G, and the total number of samples were 20 pieces for each batch and 760 pieces in 2019. The final manual samples and the in-process samples were taken during the batch productions. Demand for the hand samples is required in the quality control and the high quality of the materials can be confirmed by the hand samples. The high number of the manual samples is risky for the operators and the hazardous samples contain the toxic compounds, such as phenol and formaldehyde. The list of the hazardous materials, the aqueous concentration of phenol and the number of the hazardous hand samples can be found from the appendix 2.

The figure 11 illustrates the allocation for the total number of the hazardous hand samples and the manufacturing materials in Kitee in 2019. The most critical hand samples were taken 865 times by the operators in 2019. Second, the materials that have phenol between 1-5 % were taken 1413 hand samples in 2019. Overall, there were taken 2278 hand samples by the operators from 14 manufacturing materials in 2019.

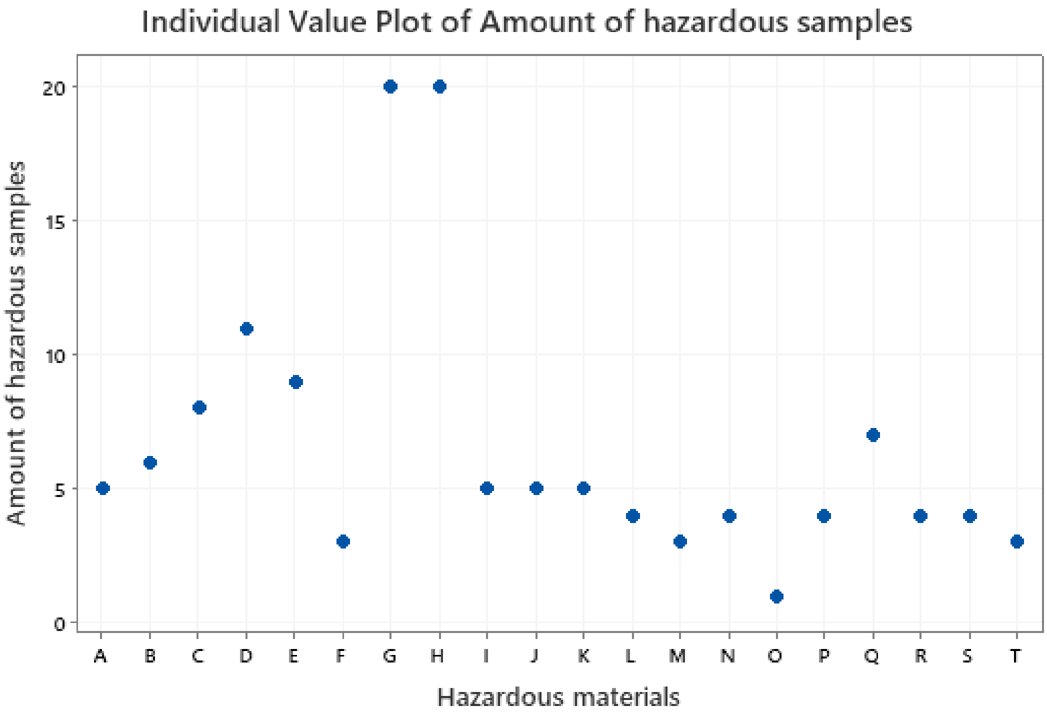


Figure 11. Total number of hazardous manual samples and materials in Kitee in 2019.

5.2 Health hazards

The purpose of this section is to introduce the health hazards chemicals and toxicity problem in the resin plant. The properties of hazardous chemicals and the physical and chemical properties will be presented in this section. Main hazardous chemical are formaldehyde and phenol at Hexion Kitee. Formaldehyde is originated in the formaldehyde in Kitee plant and phenol is purchased from the Finland and Russian.

5.2.1 Toxicity

Phenol or the derivatives are caused by the society activity and some phenol is originated from the manufacturing processes and others from natural processes. In fact, phenols are very harmful and toxic exotoxins. Phenols hold properties of carcinogenic, cytotoxic, and teratogenic. In practical, phenol can change enzyme activity and the metabolism in the humans. Health damage to the living organisms are caused by phenols and it leads to the dramatically changes in the skin, lungs, lives, and the kidneys in the long-term. Phenol can darken the skin, weaken the muscles and poisoning raise symptoms, such as headaches, nausea, and diarrhea. Also, a neurotoxic and a cytotoxic on skeletal muscle is possibly caused by phenol. (Bukowski & Adamczyk 2003, p. 1-5)

Phenol is an aromatic compound with including the hydroxyl group, phenol dissolves into water, ethanol and ether solutions, and phenol is colorless as the solid state. Phenol has a relatively high melting point, 41 ˚C. The phenol may burn, but it does not ignite easily, and the phenol storage tank may tear with contribution of flame. Phenol is a very toxic compound, and it can cause the kidney and liver diseases, the loss of eyesight. The aqueous solution of phenol over 5 % cauterize the skin, cause arrhythmias, shock symptoms, convulsions, deep unconsciousness and possibly death. The operators need to use the suitable protective clothing, safety classes and rubber cloves to avoid direct the contact of phenol, when handling chemicals or working in hazardous areas. This action saves health and lives in the long term. (Gardziella *et al.* 2000, p. 3; TTLa 2017)

Formaldehyde is as well a toxic and a carcinogen compound to humans. Formaldehyde is mainly used in the manufacturing processes, such as construction, textile, furniture, medical, chemical, and pharmaceutical industries. Therefore, formaldehyde is impacted to humans in many sectors. Formaldehyde is accepted to be a carcinogen to human. (Duong *et al*. 2011, p. 2)

Formaldehyde is an aldehyde; it is a colorless gas at the room temperature, and it smells strongly. Formaldehyde dissolves in water and organic solvents, as well. The aqueous solution of formaldehyde in 37-50 % can be called for formalin. Formaldehyde has a relatively low melting point, -92 ˚C, and it is a gas in the normal conditions. Formaldehyde is a very toxic compound, it can cause the cancer, it is toxic by inhalation and it can cauterize the skin. Formaldehyde can cause the healthy problems, such as coughing, wheezing, nausea, and skin irritation if formaldehyde presents more than 0.1 part per million (ppm). More and less, some people react more sensitively to formaldehyde than others. (TTLb 2017; American Cancer Society 2020)

5.2.2 Sampling hazards in manufacturing

Finnish law of chemicals (Kemikaalilaki 599/2013) states that the health and environment need to be protected from the chemical hazards and harms (Finlex 2020). Sampling tasks are caused hazards and harms for the manufacturing operators, and therefore any actions need to be performed in Kitee. Today, many operators handling the hazardous samples and touching a phenolic samples numerous times in manufacturing site. Handling and storing of the hazardous chemical must be completed by the Finnish law and regulations, and the manufacturing site is responsibly to follow these legislations (TUKES 2020b).

Many chemical industry companies use the hazardous chemicals, and therefore the vulnerability for the hazardous chemicals need to be considered as part of the risk assessment. The employer needs to survey all hazardous chemicals and evaluate them in the risk assessment if the chemicals are hazards for the health and safety. Further, the usage of the hazardous chemicals needs to be reduced as minor as possible in the manufacturing site. If the hazardous chemicals must use, then the safety workplace for the employees need to be confirmed. (Työsuojelu 2020)

However, the sampling is only way to verify the quality of the products and the reliability manufacturing in the chemical industry. The wet chemistry plays an important role to verify the quality management and the process capability, and the hand samples can be confirmed the quality specifications for each material and product. The operators have responsibility to pick up samples and perform the analytical task to verify the quality specifications.

6 MATERIALS AND METHODS

This section goes through strategy plan during the experimental section, the NIR spectra collection in Kitee and the NIR measurements.

6.1 Experimental procedure

Procedure plan was prepared for the experimental section to verify for all parties and clarify the instructions to be used during master thesis process. All actions were managed by the strategy plan. The following details of NIR spectra collection were considered during the experimental section:

1. Hand samples are collected
2. NIR spectra are measured for all samples
3. Wet chemistry analysis is performed by operators
4. A calibration model is computed using multivariate statistics
5. Validation testing is performed for the calibration model

Hand samples were collected from the hazardous phenolic resins and the hazardous materials have been listed in the appendix 3. The collection of the samples was managed with Excel list, in which added the hand samples with all desired details. NIR matrix was running the night and day to measure all hand samples and measurements were performed at temperature of 25 ˚C by the manufacturing operators. Furthermore, the hand samples were taken from the materials, which was not manufactured in the reactor R204 and R205. The operators picked up the samples and analyze them with NIR probe in the laboratory.

As mentioned, to real world involved practical issues, such as the instrument noise, nonlinearity between the NIR spectra and the results from the wet chemistry analyzes, the errors in reference results, the unstable samples, and the sampling errors. These factors were considered during the experimental section so that the samples collected and measured with the NIRS device at the same time. Further, the hand samples and the NIR spectra were successfully compared with each other, and there was the linear line between the NIR results and the reference results. The unstable samples and the sampling errors were considered during computing a calibration model using multivariate statistics.

6.2 Methods

6.2.1 NIR data from manufacturing reactors

NIR spectra was started to collect at the end of July in 2020 in Kitee. The NIR spectra was collected first from the batch reactor R204 (figure 12), in which the transmission probe (1) was placed in the side of the batch reactor (2). The NIR probe measured the hazardous samples and the NIR spectra was received to the NIR PC all of time during the collection time and this collection time continued to the middle of the August.

Figure 12. NIR probe (1) have installed in the side of the batch reactor R204 (2) in the manufacturing area.

Sampling plan was prepared for this experimental section to measure the NIR data and as well the wet chemistry analyzes from the hazardous materials, which have been listed in the appendix 3. The NIR spectra was decided to collect from the final samples at the temperature of 25 °C in the manufacturing. There was decided to measure the NIR data from the manufacturing batch reactors R204 and R205, which were the most properly sampling points in the manufacturing area. The sampling plan was introduced for the manufacturing operators to recording the exact sampling times for the NIR data collection list. Furthermore, all details were given to the operators to declaring the master's thesis process in Kitee. In fact, the following remarks were considered for the sampling.

1. Sample set from final samples
2. Measurements are performed at temperature of 25 °C
3. Sampling section for both manufacturing reactors
4. Sampling training for manufacturing operators
5. Sampling collection times for the list

Measurements was started up by the OPUS program in the NIR PC and allowed to store the NIR spectra to the NIR PC. The detailed process steps were performed and started to collect NIR data from the manufacturing batch reactors. Every minute the NIR spectroscopic device measured the samples and recorded the NIR spectra from them. All NIR spectra were uploaded to the local NIR PC and the OPUS software program was used to collect the NIR data. In fact, the OPUS program is the spectroscopy software for the measurements and any investigation of the NIR spectra. The OPUS program includes numerous types of the function, such as the data processing, investigation and possibly to store the results, the spectra files and any parameters. (Bruker 2020)

After first sampling section, the NIR probe was moved from the side of the reactor R204 to the side of the reactor R205 1.9.2020 at 11 AM. The NIR spectra was collected again all of time. Since the beginning of October, the NIR probe of the manufacturing laboratory was taken into use to collect the NIR spectra from the hand samples.

6.2.2 NIR data from hand samples

NIR data sampling was moved to the manufacturing laboratory to measure the hazardous samples by the NIR spectroscopy. There is the NIR probe to measure any materials in the manufacturing laboratory, which is available for the manufacturing operators. The NIR probe (1) and the sample stand (2) can be seen in the figure 13.

Figure 13. NIR probe to measure the hazardous samples in the manufacturing laboratory.

A sampling plan was prepared for this sampling section. The sampling method involved on the standard ISO/IEC 17025:2017 and the hazardous samples are picked up from the manufacturing batch reactors and the samples are treated as documented. The hazardous samples were analyzed with the cooperation of the manufacturing operators. The suitable safety classes, gloves and clothes were used during the experimental sections in the manufacturing laboratory and the protocol record was filled.

The applied apparatus and requisites are presented in the table 3. NIR transmission probe was used to measure the hazardous samples, temperature of the samples was measured with temperature gauge and a couple of the beakers glasses were used to dosing the samples. Furthermore, methanol was used to cleaning the NIR probe after the measurements in the manufacturing laboratory.

Table 3. Usable apparatus and requisites during the experimental sections.

Requisite	Details
NIR transmission probe	Matrix F
Temperature gauge	
Beaker glasses	400-900 ml

Sampling was prepared to ensure all chemicals and requisites were available in the manufacturing laboratory and the sampling plan was introduced to the manufacturing operators. In fact, the hazardous samples were picked up from the batch reactors by the manufacturing operators and analyzed them with the NIR spectroscopic probe. The manufacturing operators were trained to analyze the samples with NIR probe and record the results.

Hazardous samples were measured with the NIR transmission probe and the samples were collected from the batch reactors to the beaker glass of 900 ml by the manufacturing operators as can be seen in the figure 14. Temperature of the sample was recorded to the protocol document and then the NIR probe was placed in the middle of the sample to record the good NIR spectra and avoid to recording any noises from the laboratory area. The NIR probe analyzed the sample 5 minutes to recording the NIR spectra for the NIR PC, in which the NIR spectra are available. After the NIR analyzed the hazardous sample, then the NIR probe was sanitized with methanol of 400-500 ml a few minutes and finally the NIR probe was cleaned with a soft cloth. The cleaning was done for each sampling set, so that no any impurities influenced on the NIR spectra.

Figure 14. NIR probe is put to analyze the hazardous samples in manufacturing laboratory of the Kitee plant in 2020.

During the NIR measurement sections the analysis of the 3, 4, solids and the concentration of phenol and formaldehyde were performed on the same time and the results were recorded. These reference results were recorded during the experimental section in the manufacturing laboratory. Furthermore, regarding the standard ISO/IEC 17025/2017 the manufacturing operators recorded the material, which was measured with NIR spectroscopic probe, date, time, the amount of sample as ml, the batch number, time period for NIR measurements and temperature.

7 NIR CALIBRATION MODEL

Practical usage of NIR technology involve on the creation of the NIR calibration model, which means constructing the mathematical function by the NIR spectra set and the analysis results of the reference analyzes. In fact, there are needed a lot of number samples (20-200) to create the NIR calibration model, which fit to the data. The following figure 15 illustrates to creating the NIR model by applying the chemometric. The NIR spectra set and the reference results are the key elements of the creating the NIR model.

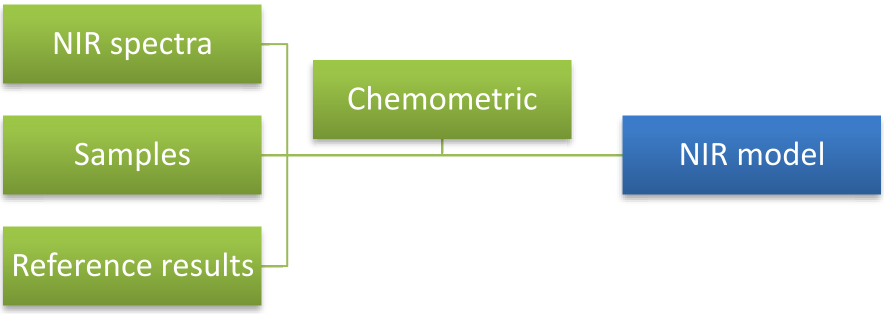


Figure 15. Creating NIR model by NIR spectra set, samples and reference results applying the chemometric.

NIR model correlates the fact of the calibration that as much the samples are collected then more accurate NIR model will be created. Moreover, of that fact, during collecting the NIR spectra set the conditions need to be standard and any variations need to be eliminated, if to create the very accurate NIR model to predict the future samples.

Nowadays, the creation of NIR model is constructed by the analytical program and that constructs the NIR model optimizing the best combination of the algorithms and the wavenumber regions. First, the pretreatment needs to be done for the NIR spectra set and all rejected NIR spectra should be deleted. The rejected NIR spectra are such as spectra, which are diverging from the average NIR spectra. The goal is to get the good NIR spectra set, which can be used to create the NIR calibration model. Second, the pretreatment algorithms and the wavelength need to be selected. In fact, the usable algorithms can be many available, such as the standard normal distribution. The regions of the wavelengths are selected by the functional groups of the molecules and their absorbance responses. Final, the analytical program optimizes the best combination to create the NIR calibration model.

7.1 Analytical program

OPUS spectroscopy software is one of application program to collect the NIR spectroscopy data, processing of NIR and Raman Spectra and includes many software packages. The OPUS package involving many types of measurements, it is capable to processing and evaluating the NIR spectra. Furthermore, OPUS spectroscopy software program includes the library search and identification capability, the database actions for storing the any results, the NIR spectra files and the measurement parameters, as well. (Bruker 2020)

This analytical program consists of file processing, edit possibility for the created files, many measuring and manipulating options, and evaluating possibility to creating the method to measure the unknown samples by the calibration model. OPUS program versions are many available in market, but it should use the newest program to process the NIR spectra and measure the unknown samples in 10 seconds.

Files can be loaded or unloaded in the OPUS program, create the data point table and there is the print possibility. The NIR spectra is saved to the OPUS program during the NIR measurements and therefore the NIR files can be easily loaded to investigate any NIR spectra later. All NIR spectra files can be printed in PDF form and saved to any folder.

First, manipulating the NIR spectra many corrections, normalization, extrapolation and noise generation can be done. OPUS program enables to manipulate the NIR spectra in many options, such as the baseline correction, the straight-line generation, averaging and many others. Second, evaluating enables to measure the unknown samples by the quantitative analysis, so called QUANT 1 or QUANT 2 method, which are used to measure any property of the samples. In fact, using with some QUANT model the property of the sample can be measured with the NIR spectroscopic. Each material needs 1 QUANT model for 1 measuring property, such as the concentrations of any component or the physical property. Therefore, there are many QUANT models in each material to measure the unknown samples.

7.2 Procedure to create NIR model

Construction of NIR calibration model begins with collecting the calibration samples and determining each component of various concentrations by some analytical method in the technical laboratory. Further, the NIR spectra are also needed, so that these calibration samples and their spectra can be compared in the analytical program to create the NIR calibration model. (OPUS 2004, p. 192)

In fact, there is needed one peak in the spectra to investigate the concentration of each component and this procedure can be done by the various ways, such as baselines, intensity or area. The peak area in the spectra is needed to be determined, then a calibration function shall be fitted to the collected data. The calibration function can be created by the linear, quadratic or polynomial function, but the best is to use the linear function in many cases. The created calibration NIR model is used to predict the concentrations of the future samples by the NIR technology. (OPUS 2004, p. 192)

First, it's needed to open *Setup Quant Method* in OPUS program and specify the names and units of the desired components, select the calibration spectra set and enter the component values of the analytical method. Second, it needs to define a peak in the spectra for each component and select the type of the calibration function, such as the linear, quadratic or polynomial function. However, *Quant Method Analysis* is not suited for overlapping bands, so therefore for each component need to be found a clear isolated peak in the spectra. In fact, there are many various methods for calculating the band intensities, either the peak area or the peak height is used. Finally, the OPUS program calculates automatically the calibration function and the results are shown as the table and the diagrams.

In theory, the calibration functions are saved as Y = f(X) where the Y are the values obtained by the fit and X is the peak size obtained from the NIR spectra.

The correlation coefficient r can be used to indicate the quality of the NIR calibration model. This correlation coefficient is a good estimation to evaluate the useful of the NIR calibration model. In fact, the correlation coefficient needs to be close to 1.0, so that the calibration model fits to the data. The equation of the correlation coefficient (15) r is represented below.

$$\mathrm{r} = \frac{\sum((\mathrm{Z_i}-\mathrm{Z_m})(\mathrm{Y_i}-\mathrm{Y_m})}{\sqrt{\sum(\mathrm{Z_i}-\mathrm{Z_m})^2\sum(\mathrm{Y_i}-\mathrm{Y_m})^2}} \tag{15}$$

Where Z means the true concentration of the components and Y means the predictive concentrations of the components, whereas m as subscript is the respective average value.

Furthermore, the standard deviation σ is used to present the difference between predicted and the true value. There is an approximated 68 % probability that the concentration of the predicted sample involving to an interval of the predicted value plus or minus σ. The equation of sigma (16) is presented below.

$$\sigma = \sqrt{\frac{1}{M-f}\sum(Z_i - Y_i)^2} \tag{16}$$

Where M means the number of calibration samples, f means the degree of freedom (linear 2, quadratic 3, cubic 4), Z means the true concentration of the sample and Y is the predicted concentration of the sample.

7.3 Creation of NIR model

First steps to create of NIR calibration model is to select the properly materials and their properties. During the master thesis process have been collected NIR data from 19 various resins products by the NIR probe in the manufacturing and laboratory area. Further, there have been done many reference analyses in the laboratory, such as the 3, 4, free aqueous concentrations of phenol and formaldehyde, which have been listed to Excel list to manage this collection of NIR data. However, many of these resins' materials are not the so hazardous materials consisting of high aqueous concentrations of phenol and formaldehyde compounds. Therefore, there is a need to filter the properly materials, which are hazardous materials for the manufacturing operators.

NIR spectroscopy data was collected 4 months from August to December and during this time was collected 190 NIR spectra from various hazardous resin materials by NIR technology. In fact, NIR data was collected 55 items by the NIR probe of the manufacturing area and 180 items by the manufacturing laboratory. The manufacturing batch reactors R205 and R205 were used to collect NIR data from the real process conditions and the last NIR data were collect with the NIR probe of the laboratory. The materials of T, R and U were selected to construct the NIR models and each material shall be many NIR models depending on the analyzable properties in the manufacturing.

Material of coating resin T has 4 property (1, 2, 4 and 3) to be analyzed in the manufacturing, whereas the phenol resins R and U have 3 or just 4 to be analyzed. For each property needs to be created the NIR model to predict their values with the NIR technology. The selected materials and their analyzable properties are presented in the table 4. This table shows that there is the need to create 7 NIR models to measure the properties of these resin materials.

Table 4. The analyzable resin materials and their measurable properties.

Material	**T**	**R**	**U**
Properties	1	3	3
	2		4
	3		
	4		

NIR model was constructed for each material of the analyzable property in the application program of OPUS 7.5. As the collected NIR spectra were not so accuracy as expected, then was used setup QUANT 2 method was used for creating 7 NIR models in the OPUS program. This setup QUANT 2 method enabling to create the accuracy NIR models, so that the models can be used to predict the any property using with the NIR technology. However, another setup QUANT 1 method was not used this time, as it cannot create the accuracy NIR models because of not accuracy NIR spectra set was not collected with the NIR probes in Kitee.

First, the desired components, spectra set, and parameters were determined to the OPUS program and then the setup quant 2 method was optimized the best combination for creating the NIR models. While optimizing the best combination of the models, there was the preprocessing setups, such as the first derivate and the vector normalization. These processing setups were determining the best combination to create the good NIR model for each material. After the optimization, the program proposes the best calibration regions of the wavelengths and the NIR calibration model. Further, the model shows the predicted values of the NIR technology and the reference values, as well.

The created NIR models were quite goods, even though the samples and the NIR spectra were not collected as much as expected. The following table 5 presents the NIR models and their details, such as the collected NIR spectra set, datapoints, samples, optimized calibration regions as the wavenumber and the correlation coefficient for each NIR model. In fact, approximately 5-6 NIR spectra were used to create the NIR calibration model for each resin material and the correlation coefficients varied from 0.44 to 0.99. As discussed in the subchapter 7.2, the correlation coefficient is a good estimation to evaluate how useful the created NIR calibration model is to predict the samples with the NIR technology.

Table 5. The created NIR models and their details.

NIR model	Spectra	Datapoints	Samples	Calibration regions	Corr. Coeff.
T – 1	6	171	6	6102-5446	0.70
T – 2	6	15	6	6846-6900	0.66
T – 4	6	2074	6	4000-12000	0.84
T – 3	6	2074	6	4000-12000	0.43
R – 3	16	2074	16	4000-12000	0.69
U – 3	5	2074	5	4000-12000	1.00
U - 4	5	2074	5	4000-12000	0.44

8 RESULTS AND DISCUSSION

This section goes through the results of the experimental section involving the assessments of the NIR calibration models, accuracies of the NIR process values comparing for the reference results and evaluating of the NIR spectra sets.

8.1 Comparison of reference and NIR results

Hazardous resin materials T, R and U were selected to compare the reference results to the NIR results, which all were measured with the NIR technology in the Kitee plant. Only just these materials had enough data to analyze and compare the results after the experimental section during this master thesis process. The data was collected 5 samples to include the laboratory analyzes of 1, 4, 3 in the Brookfield method at 25 °C and 2 for the resin material of T. For the resin material R just measured the 3 in the Brookfield method with the temperature of 20 °C in the laboratory and the data was collected 16 samples. The samples of the resin material U were collected 5 pieces and the 4 and 3 in the Brookfield method were measured with the temperature of 25 °C. All results of refence and NIR are shown in the appendix 4.

8.1.1 Material T

NIR technology is able to measure the properties of 4, 2, 1 in accuracy for the resin material of T. The results are shown that the concentration of 1 can be measured with the NIR technology as accuracy than with the reference analyzes. The difference of the means between the reference and the NIR mean just 0.01 in the resin material T and the difference of the deviations is just 0.01. The property 4 for the resin material of T can be measured with the NIR technology in more accuracy than the property of 1. In fact, the deviation with the NIR technology is lower than in the reference results. The deviation in the reference analyzes was 0.04, whereas it was 0.03 in the NIR results. This outcome provides that the 4 of the T can be measure more accuracy with the NIR technology than with the old reference analyzes. Moreover, the 2 can be measured with the NIR technology in a more accuracy than measured with the reference analyzes. The results are shown that the deviation of 2 measured with the NIR technology is lower than measured with the reference analyzes methods. However, the 3 of T the NIR technology cannot be measured so accuracy than expected and the ones of the NIR process values were too far from the reference values. The mean and deviation results of T are presented in the table 6.

Table 6. Mean and deviation comparison of the resin material of T.

Material	Analysis	Reference Mean	NIR Mean	Reference Deviation	NIR Deviation
T	3	94.87	95.87	6.41	5.72
T	4	1.87	1.90	0.05	0.04
T	2	49.45	50.40	0.16	0.07
T	1	0.25	0.25	0.02	0.02

Hazardous samples were measured with the NIR technology and the NIR spectra are shown that the NIR spectra can be distributed into 2 categories depend on the shape of the NIR spectra. The NIR spectra for the resin material of T are presented in the appendix 5. Despite many NIR spectra of the T, the NIR spectra are comparable for each other's and the results are also provided that variety can be managed better using with the NIR technology than measured with the reference analysis. The comparable 2 NIR spectra are presented in the figure 16. There were noted some noises in the NIR spectra region of 14000-8000 cm^{-1}, 7200-6800 cm^{-1} and 5000-4000 cm^{-1}, but not good reason was not observed. This noise shall be originated from the NIR device in the technical laboratory.

Technical literature and the optimized NIR model are shown that the amount of the 1 can be measured in the NIR spectra region of 5950-5920 cm^{-1}. Therefore, the amount of the 1 in the hazardous samples is directly proportional to the NIR absorbance in this NIR spectra region and the aromatics molecules are vibrated. However, the results are provided that the noises in the NIR spectra are caused more variety to the measurements than measured with the reference analysis method in the technical laboratory. Table 6 is also shown that the deviation of the NIR higher than the deviation of the reference analysis.

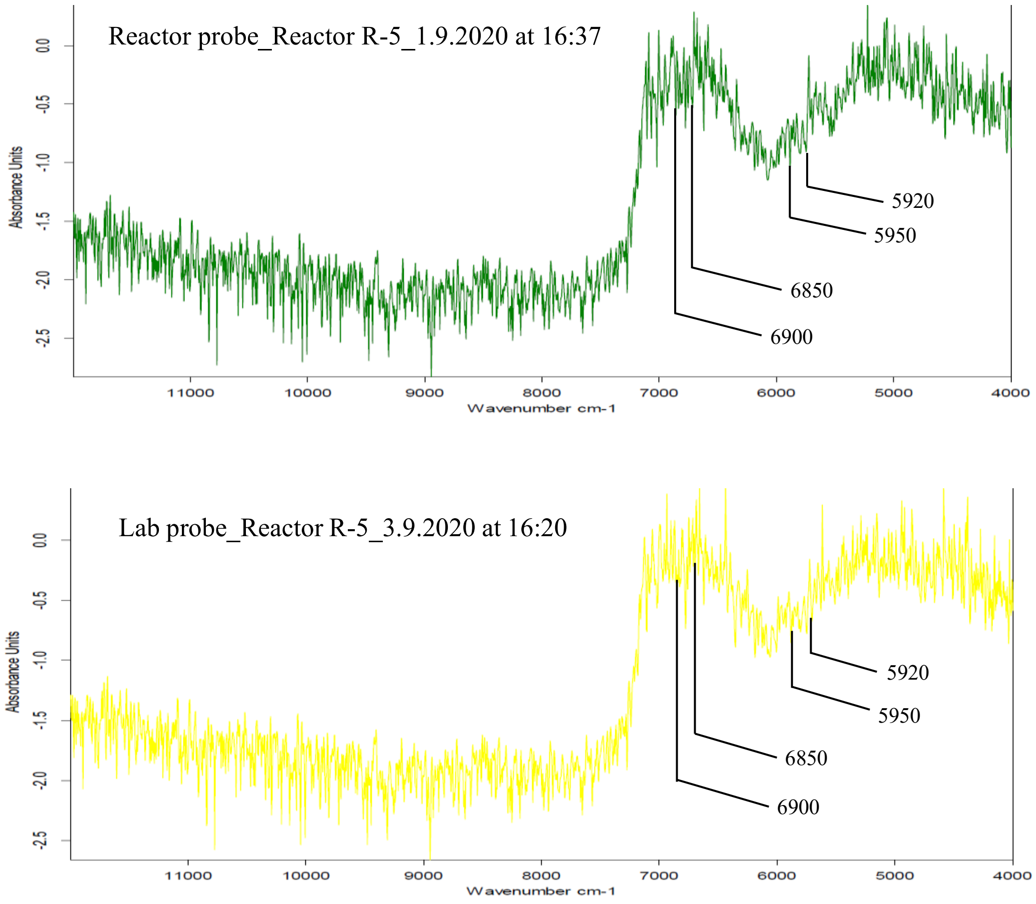


Figure 16. Comparable NIR spectra set for the hazardous resin material of T.

2 is measured with the NIR using with the NIR spectra region of 6900-6850 cm^{-1} and the 2 is directly proportional to the NIR absorbance. The water molecules are vibrated in this NIR spectra region and are provided that the measurement of the 2 is based the vibration of the water molecules in the samples. In fact, the 2 can be measured with the NIR technology a more accurately than measured with the reference analysis method, and the results in the table 6 are provided it.

The 3 and the 4 of T is measured with the NIR technology using with the NIR spectra region of 14000-4000 cm^{-1}. There was not found a more accuracy NIR spectra region to be used in the NIR technology and the NIR models for each property were optimized using with this NIR spectra region.

8.1.2 Material R

Property 3 of resin material R can be measured both with the NIR technology and the reference analyzes based on the results. However, the 3 results measured with the NIR technology were outstanding 0.12-3.09 from the results of the reference analyzes and are shown, that the reference analyzes results differs from the results measured with the NIR technology. More detailed analysis is shown that the deviation of the NIR results is much lower than the deviation of the reference results and using the NIR technology to measure the 3 of the resin material R will be manage better the deviation of the R.

Reference mean and the NIR mean are given almost the same value and then is proved that the NIR technology is able to measure the 3 of R as accuracy than with the reference analyzes. The mean and deviation of the reference and NIR results are presented in the table 7.

Table 7. Mean and deviation comparison of the resin material of R.

Material	Analysis	Reference Mean	NIR Mean	Reference Deviation	NIR Deviation
R	3	45.07	42.14	1.30	1.14

Property 3 was only one property for the resin material of R and the optimized NIR model was shown that there is not the exact NIR spectra region available. The figure 17 is shown the part of the NIR spectra and all NIR spectra can be found from the appendix 5. There is noted a lot of number of noises from the recorded NIR spectra and not the good reasons were not found for this recognition. In fact, it’s a sum of many factors including the noise of the NIR device and the low 3 level in the samples. There was observed during the experimental section that the samples be able to accuracy measured with the NIR, if the property 3 of the resin material is too low. The resin material of R is specified to be 30-80 mPas in the manufacturing and this range is the comparatively low for the others resin materials in Kitee site.

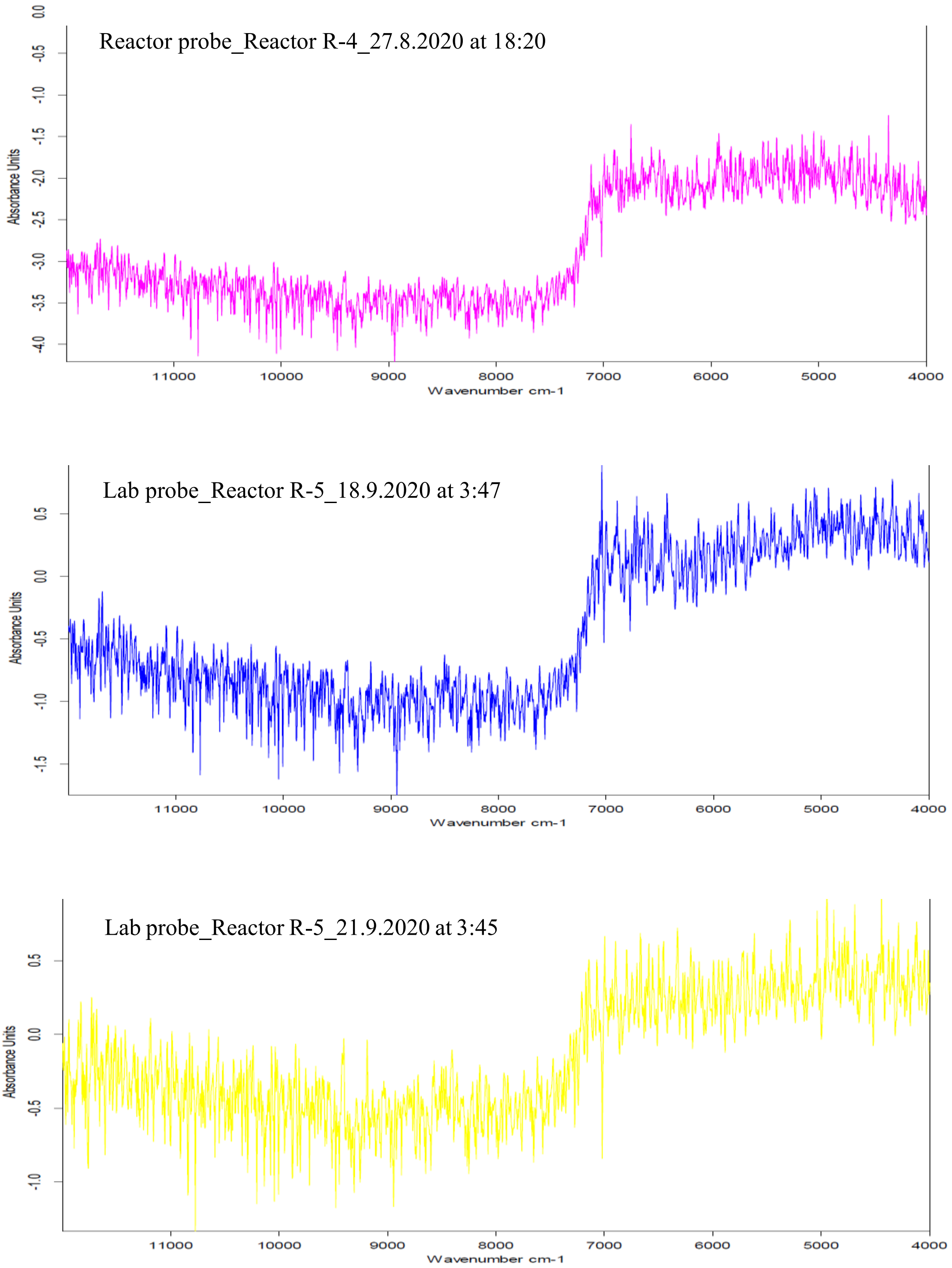


Figure 17. Comparable NIR spectra set for the hazardous resin material of R.

8.1.3 Material U

Reference analyzes for the property 3 and the 4 were measured in the temperature of 25 °C for the resin material U and data was collected 5 samples in the Kitee plant. First, the results are shown that the viscosities measured with the NIR technology were outstanding 0.001-6.3 mPas from the reference results, but overall the NIR technology is able to measure the property 3 of U and most of the viscosities measured with the NIR technology follows the results measured with the reference analysis. However, the deviation of the samples measured with the NIR was lower than the deviation of the samples measured with the reference analysis methods. This fact provides that the NIR technology is a more suitable to analyze the property 3 of the U in the manufacturing.

Second, the values of the 4 measured with the NIR technology were outstanding 0.001-0.132 from the reference results. The 4 can be measured with the NIR technology and its accuracy is very high compared the results of the reference analyzes. However, the deviation of the samples measured with the NIR technology was higher than the deviation of the samples measured with the reference analysis. The means of the samples are the almost same and there is the difference 0.029 in the 4. The means and deviations of the U are presented in the table 8.

Table 8. Mean and deviation comparison of the resin material of U.

Material	Analysis	Reference Mean	NIR Mean	Reference Deviation	NIR Deviation
U	3	398.90	407.53	15.11	14.84
U	4	7.78	7.93	0.07	0.04

Measured NIR spectra set of the resin material of U are shown that there are not many noises than comparatively to others measured NIR spectra set. The comparable NIR spectra of the resin material U are presented in the figure 18 and all NIR spectra can be found from the appendix 5. The noise can be found from the NIR spectra region of 14000-7000 cm^{-1} and 5000-4000 cm^{-1}. The good, rationalized reasons are the noise of the NIR device and the air bubble in the samples as explained in the previous sections.

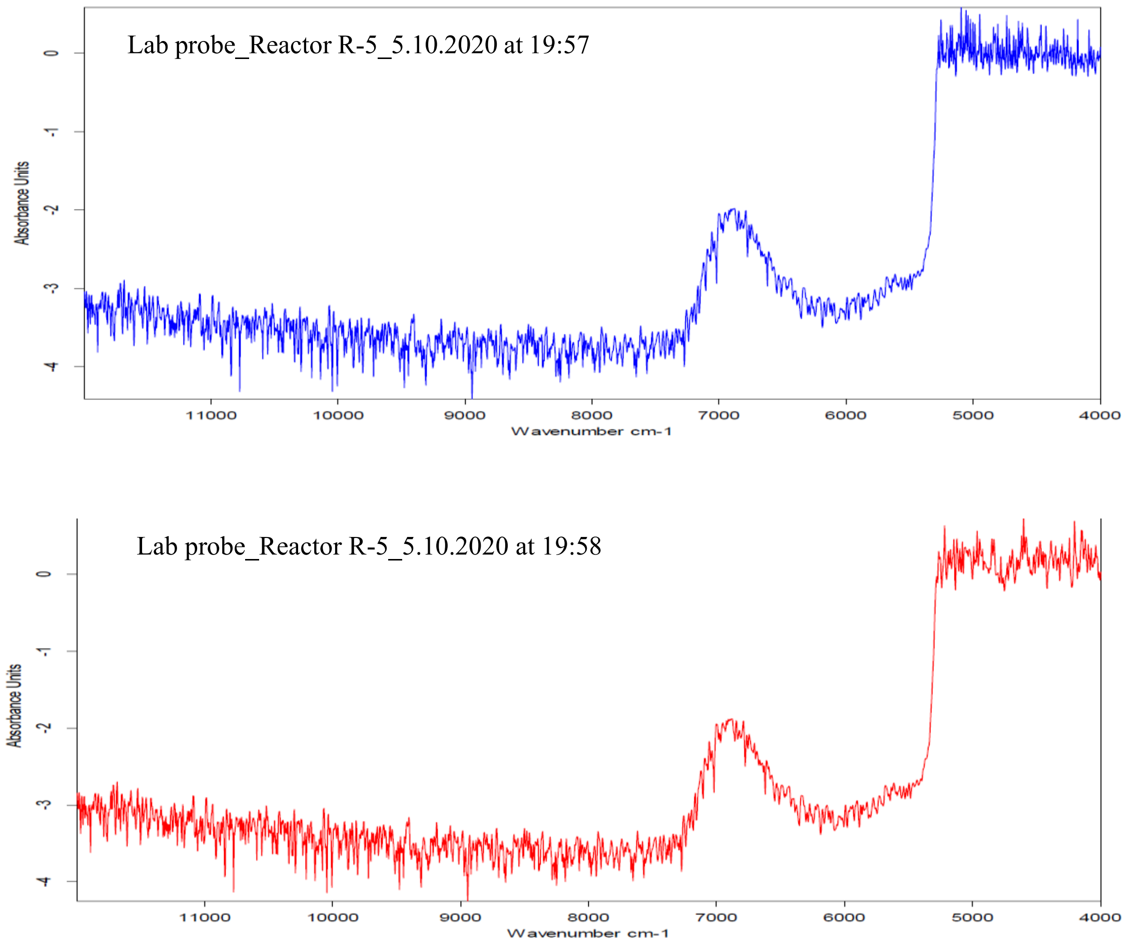


Figure 18. Comparable NIR spectra set for the hazardous resin material of U.

The properties 3 and 4 of the resin material U are measured with the NIR using with the NIR spectra region of 14000-4000 cm^{-1}. The NIR models were optimized for this NIR spectra region and the results are still shown that the NIR technology is suitable to measure the properties 3 and 4 of the resin material U. The NIR spectra set are accuracies to comparatively to others the NIR spectra set. There were recognized that the property 3 is a good indicator for the accuracy of the NIR spectra. In fact, as more property 3 in resin material is measured then more accuracy NIR spectra is achieved during the experimental tests.

8.2 Evaluation of NIR results

8.2.1 Assessment of significance with two sample t-test

Comparison of the samples was used the two samples t-test to evaluate the results of significance. T-test of the two samples can be applied for the mean comparative experiments, in which are comparing the options each other's. In fact, the means of the sample sets are comparing in this assessment of the significance evaluation using with the t-test. There are 4 stages in the comparative experiments and the stages are following.

1. Setting the hypotheses
2. Determining the risk level
3. Determining the decision criterion
4. Conclusion, which hypothesis is correct

Hypothesis is the proposition based on the parameters of the probability and there are 2 hypotheses available in the comparative experiments. Null hypothesis and alternative hypothesis; the null hypothesis proposes that there are not markable difference between two sample shots based on any properties, whereas the alternative hypothesis proposes that there are markable difference between two sample shots based on any properties. The hypotheses can be settled in two way; compare a one shot to the constant value or compare two shots with each other.

Means or deviations are generally tested in the comparative experiments and the experiments are used to prove the hypotheses to be correct or incorrect. If the null hypothesis cannot be proved to be incorrect, then it is accepted to be correct in statistically. In fact, the null hypothesis is proved to be correct with the enough statically accuracy.

Alfa-error (α) or Beta-error (β) are used in the comparative experiments. The alfa-error (α) indicates that the null hypothesis is rejected, even though its correct or the alternative hypothesis is accepted, though the null hypothesis is correct. The Beta-error (β) indicates that the null hypothesis is not rejected, even though its incorrect or the null hypothesis accepted, though the alternative hypothesis is correct. The risk levels are indicated as the probabilities and the risk levels need to be selected. In fact, the selection of the risk level is always difficult and its subjectively.

Comparing the reference and the NIR results need to be determined are the differences markable in statistically. If the variance is not known, then t-test can be used to investigate the difference of the means. In fact, the t-test examines the differences of the means and are these means markable in statistically. Usable equation of the t-test (17) is presented below.

$$t_0 = \frac{\tilde{y}_1 - \tilde{y}_2}{S_p\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \tag{17}$$

where	t_0	is the result of the t-test
	$\tilde{y}_x$	is the mean of the sample set
	n_x	is the number of the samples

With the equation (17) is calculated the value of the t-test. This value is then comparing to the critical value of the t-student in distribution based on the degree of freedom. The degree of freedom is calculated with the following equation (18).

$$v = n_1 + n_2 - 2 \tag{18}$$

where	v	is the degree of freedom
	n_x	is the number of the samples

Decision criterion is needed to be accepted or rejected the hypotheses and it take account the risk level, the sample set and the variation of the investigation property. There is the properly decision criterion, which is calculated and then the decision criterion is comparing to values of the probability distribution. Finally, the decision is made based on the value of the decision criterion. The null hypothesis is accepted, if the calculated decision criterion is the lower than the value of the probability distribution, or alternatively the null hypothesis is rejected, if the calculated decision criterion is the higher than the value of the probability distribution.

8.2.2 Comparison of reference analyzes to NIR results in 2020

Comparison was done for the resin materials T, R and U, since the data was successfully collected from August to December and these materials had enough data to create the NIR models and therefore the NIR results available. First, the means and deviations were calculated for each sample sets including both the reference and NIR measurements. The means and deviations are presented in the table 9. The results are shown that using with the NIR technology in the manufacturing the deviations are lower than analyzed with the reference analyzes. In fact, the quality analyzes for the 3 of the R, T and U are recommended to be done with the NIR technology. There is not matter which analysis method is used, the reference or NIR analysis is applied for the 4 or the 2. Still, the analysis of the 1 is recommended to do with the NIR technology, and the results are provided that the deviation of the sample set is lower than to be analyzed with the reference analysis method.

Table 9. Comparison of the reference and the NIR analysis in the Kitee plant 2020.

Group 1 (Reference)	**T-1**	**T-2**	**T-4**	**T-3**	**R-3**	**U-3**	**U-4**
Mean	0.25	49.45	1.87	94.87	45.07	398.90	7.78
Deviation	0.02	0.16	0.05	6.41	1.30	15.11	0.07
Number of samples	6	6	6	6	16	5	5

Group 2 (NIR)	**T-1**	**T-2**	**T-4**	**T-3**	**R-3**	**U-3**	**U-4**
Mean	0.25	50.40	1.90	95.87	45.93	407.53	7.93
Deviation	0.02	0.07	0.04	5.72	1.14	14.84	0.04
Number of samples	6	6	6	6	16	5	5

Means difference	0.00	0.94	0.03	0.99	0.86	8.63	0.15
Difference	-2 %	-2 %	-2 %	-1 %	-2 %	-2 %	-2 %
Degrees of freedom	10	10	10	10	30	8	8
Sp	0.02	0.12	0.04	6.08	1.23	14.98	0.06
t-test result	-0.41	-13.37	-1.28	0.28	-1.97	-0.91	-4.35
Critical t-value	2,228	2,228	2,228	2,228	2,042	2,306	2,306
Accepted hypothese	Ho	Ho	Ho	Ho	Ho	Ho	Ho

T-test results of the two sample shots are presented in the table 9 based on the NIR experimental test in the Kitee plant 2020. First, it can be provided that the means differences are the most minor with the analysis of the 1 and the 4 in the resin material of T. Completed t-test is shown that these are the most statistically significant, since the t-test results are not exceeded the critical t-values. The critical t-values have taken from the probability distribution of the t-studentin. However, the table 9 is provided that the null hypothesis is accepted for all analysis of the resin materials and therefore there is no markable difference between the reference analysis and the NIR analysis. Sum up the results of the t-test, t-test is provided that the NIR technology is suitable for all analysis of the resin materials.

8.2.3 Process capability analysis

Process is capable, if it produces the materials or products that meet the specified specifications, and it is stable in statistically. The target specifications are determined by the nominal value and the tolerance, and the upper specification limit (USL) and the lower specification limit (LSL) are used to determine the tolerance of the process. In fact, the distribution of the capable process is laying in the middle of USL and LSL. There are the ability index C_p and another ability index C_{pk}, which is paying attention for the mean of the sample set. The figure 19 is demonstrated the distribution of the capable process and the actual process values are distributed.

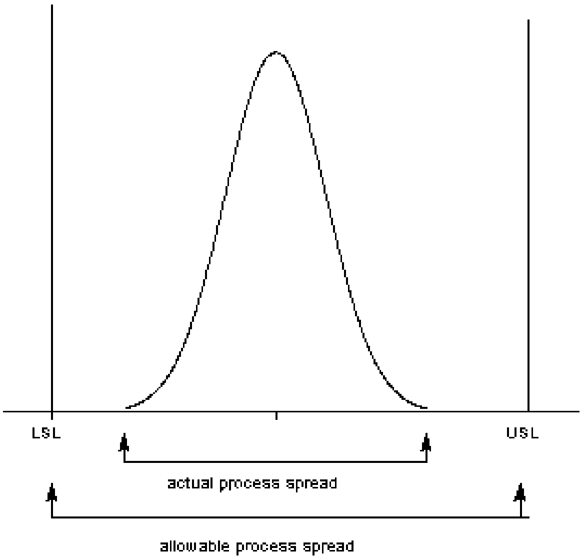


Figure 19. Distribution of the capable process.

General, most of the process values is 3σ far from the mean of the sample set, therefore variability of the process values is approximately 6σ. The process is capable, if its tolerance is wider than that 6σ. The ability index C_p is calculated with the following equation.

$$C_p = \frac{USL - LSL}{6\sigma}$$

where	C_p	is the ability index
	USL-LSL	is the tolerance of the process
	σ	is the deviation of the process

Moreover, another ability index C_{pk} is calculated with following equation

$$C_{pk} = MIN\left[\frac{x - LSL}{3\sigma}, \frac{USL - x}{3\sigma}\right]$$

Process capability analysis was done for the NIR methods to be investigated the sigma levels and the process capability. This master's thesis is going to find out is the NIR technology suitable to improve the sigma level for some analysis in the manufacturing site.

The procedure was done for the NIR analysis and the process capability results are presented in the table 10. The results are shown that the 3 analysis process of the T can be upgraded into the sigma level 3σ using with the NIR technology in the manufacturing. This is the acceptable process capability stage, and it is provided that the analysis process is the capable. Moreover, the 4 analysis process of the U was upgraded into the sigma level 4σ using with the NIR technology. However, there was not matter for the analysis process of the 4 for the T and the 3 of the U. The sigma level was not upgrading, if is used the NIR technology for the analyzes.

The NIR technology has the remarkable significant for the analysis processes in the manufacturing site and improve the process capability in overall. The most improving target are the analysis processes of the 3 for the T and the 4 for the U. Surely, it would be useful to use the NIR technology to measure these properties of the resin materials in the manufacturing. Moreover, the results are provided that the NIR technology is suitable for all these analysis processes and it is the acceptable technology.

Table 10. Process capability tests for the NIR analysis.

Group 2 (NIR)	**T-1**	**T-2**	**T-4**	**T-3**	**R-3**	**U-3**	**U-4**
C_p	NA	**4.513**	**0.871**	**0.873**	**7.292**	**0.786**	**1.563**
C_{pk1}	NA	**22.096**	**1.729**	1.506	**4.464**	1.741	**5.731**
C_{pk2}	NA	-13.070	-1.729	**0.241**	9.938	**-0.169**	-2.605
Sigma level	NA	6σ	2σ	2σ	6σ	2σ	4σ
Inside the spec	NA	99.999	95.46	95.46	99.999	95.46	99.9937
DPMO	NA	0.002	45400	45400	0,002	45400	63
Inside the spec (1,5σ move on mean)	NA	99.999	69.15	69.15	99.999	69.46	99.379
DPMO (1,5σ move on mean)	NA	3.4	308500	308500	3.4	308500	6210

8.3 Evaluation of the NIR models

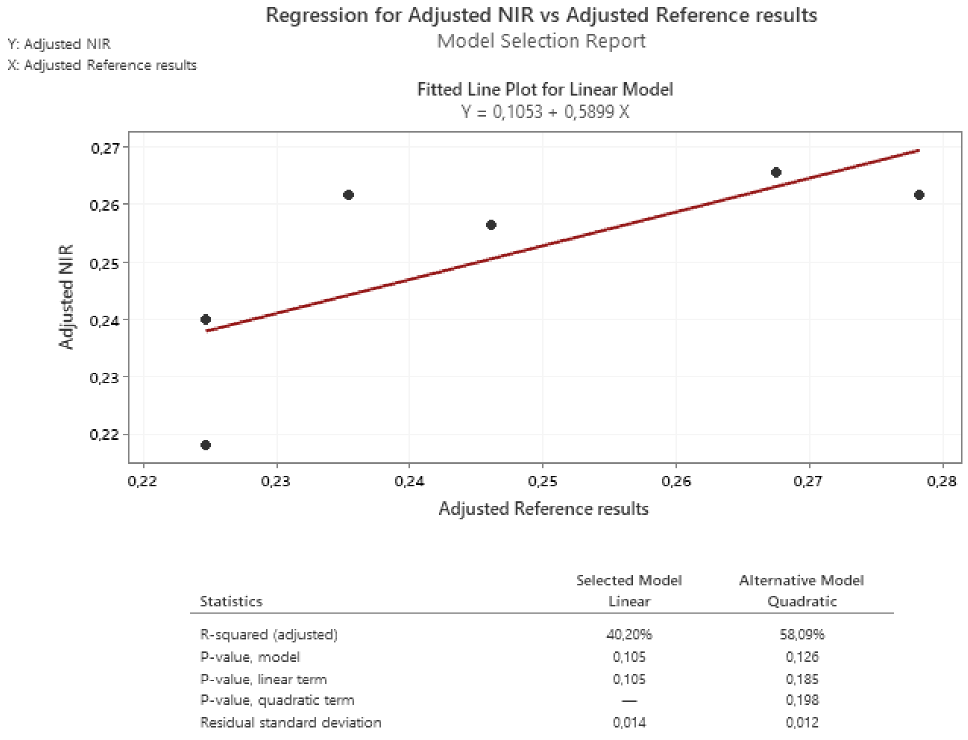
This evaluation section goes to analyze the created NIR models and to be identified the NIR models. Process knowledge, design and development are the main arguments to identify the NIR models and therefore optimizing the performance of the NIR models. In fact, the construction of the NIR model is hard to solve and practical completion is preferred. First, there is needed to select the properly construction model, identify the parameters for the model and finally validate the model. If the properly model is found, then performance of the model is good and validated to be used. However, if the model is not good, then more data is needed to collect and fit the model for the data.

Regression analysis of the NIR models was performed with the Minitab application and the simple regression was used for. The continuous variables are the NIR results and the reference results, the type of regression model was selected by the Minitab application and the test setup was used Alpha 0.05. The models are statistically significant, if p-value is below 0.05.

8.3.1 NIR models for the T

First under review is the resin material of T, which created the NIR models to be predicted the 3, 2, aqueous concentration of 1 and the 4 using with the NIR technology in Kitee plant. All NIR models were created by the OPUS program, which optimized the NIR models to predict these properties of resin material of T. This section goes to discussion on the NIR models and their accuracies to predict the real values.

The NIR model to predict the property 1 of T is presented in the figure 20, in which included p-value for the model, R-squared and the residual standard deviation. The results are shown the NIR model is not accuracy to predict the property 1 of T, since the P-value is higher to 0.05 and therefore is not the statistically significant to predict the property 1 of T. If the P-value would inside 0.05, then NIR model would be used to measure the hazardous samples of T and to be implemented to manufacturing site.

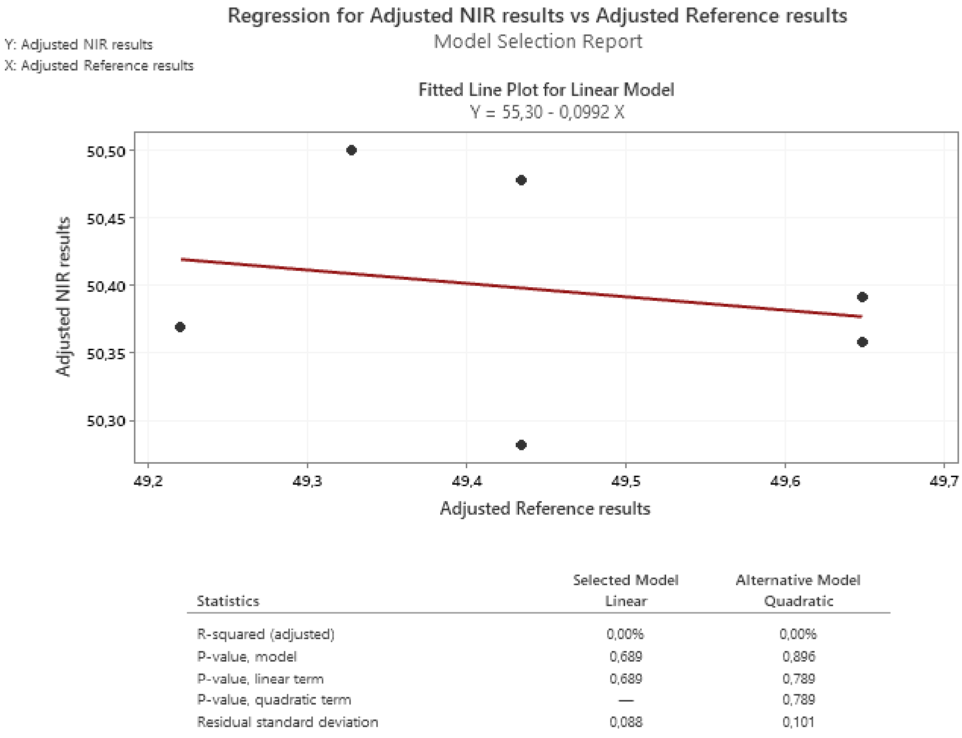


Statistics	Selected Model Linear	Alternative Model Quadratic
R-squared (adjusted)	40,20%	58,09%
P-value, model	0,105	0,126
P-value, linear term	0,105	0,185
P-value, quadratic term	—	0,198
Residual standard deviation	0,014	0,012

Figure 20. Fitted line plot for NIR model to predict the 1 of T.

Model was created using the calibration region of 6102-5446 cm^{-1}, because the literature was given the strict NIR spectra region to vibrate the relevant CH (aromatics) bonds and therefore is the most useful NIR spectra region to be used. The correlation coefficient was relatively high 0.7 and R-squared is 49.20 %, so is the statistically significant to predict the real values. If used the quadratic model, then the model fits better to the data. RMSE (Root Mean Squared Error) for this model was 0.0167 and the residual are extraordinary, so are given the statements that the model structure is correct. However, there is not enough data to make decision the NIR model accuracy to predict the aqueous concentration of 1.

The NIR model for the 2 of T was created and the results of the NIR model are presented in the figure 21. The results are shown the P-value for this NIR model is 0.689, which is provided that the NIR model is not able to predict the 2 of T using with the NIR technology. In fact, there is not the correlation between the reference and the correlation coefficient for this model is only 0.66.

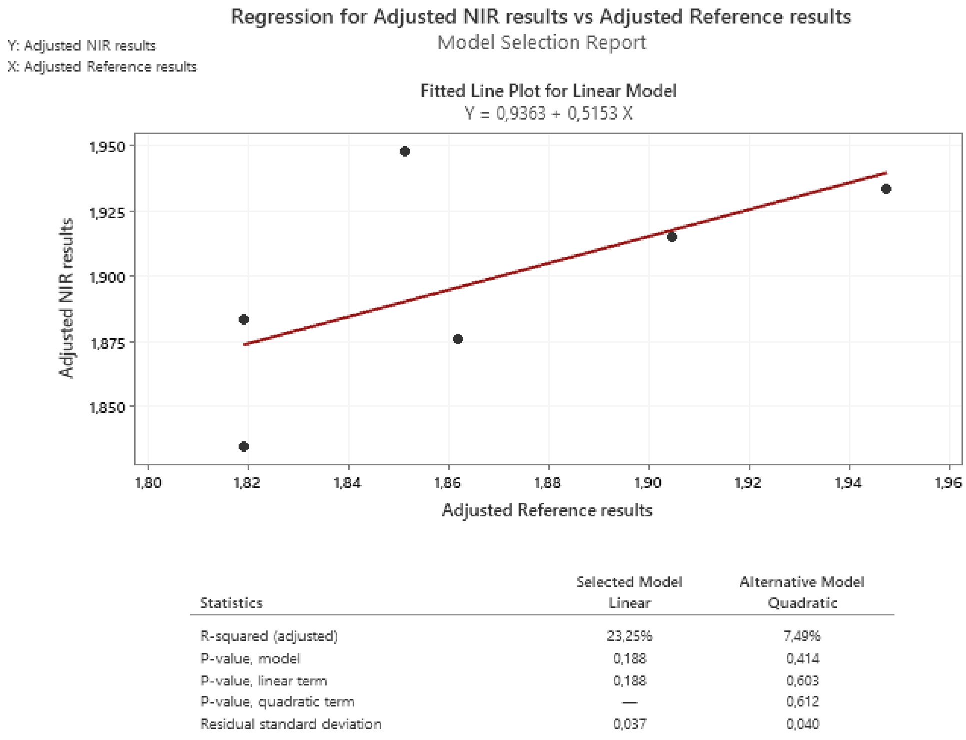


Statistics	Selected Model Linear	Alternative Model Quadratic
R-squared (adjusted)	0,00%	0,00%
P-value, model	0,689	0,896
P-value, linear term	0,689	0,789
P-value, quadratic term	—	0,789
Residual standard deviation	0,088	0,101

Figure 21. Fitted line plot for NIR model to predict 2 of T.

NIR spectra region of 6846-6900 cm^{-1} was used to create this NIR model and the literature was provided that the water molecules are vibrating. In fact, the measurement of 2 is based on the vibration of the water molecules using with the NIR technology. However, this NIR model is provided that it is not predicted accuracy the 2 of T, even though the reference and the NIR results are like similar. More hazardous samples are needed to collect and analyze, if the NIR model is capable to predict the 2 of T using with the NIR technology. 25-40 samples are needed to be created the more accuracy NIR model to predict the 2. RMSE for this model was 0.131 and the residuals are the normal probability distributed, which is provided the model structure is good to predict the 2 of T and there are not any outliers.

The NIR model for the 4 of T is presented in the figure 22. P-value for this linear NIR model is 0.188, which is provided that the NIR model is not enough accuracy to predict the 4 of T. The correlation coefficient was 0.84 and the squared R was 0.2325 for this NIR model.

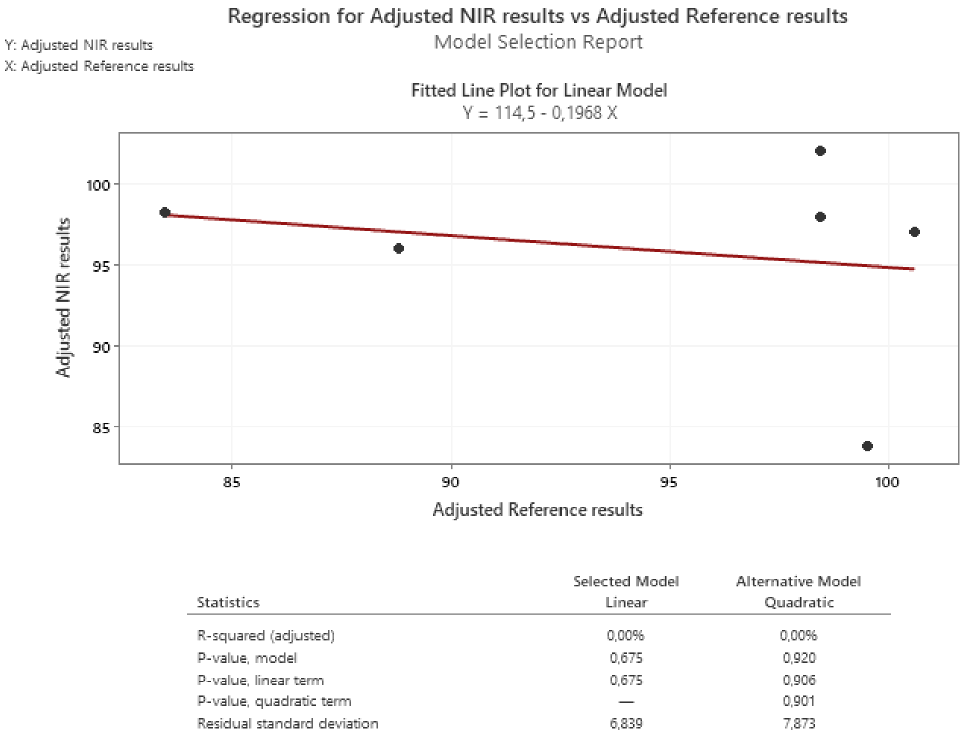


Statistics	Selected Model Linear	Alternative Model Quadratic
R-squared (adjusted)	23,25%	7,49%
P-value, model	0,188	0,414
P-value, linear term	0,188	0,603
P-value, quadratic term	—	0,612
Residual standard deviation	0,037	0,040

Figure 22. Fitted line plot for NIR model to predict 4 of T.

The NIR calibration region of 4000-14000 cm^{-1} was used to create the NIR model for the 4 of T and the RMSEE was 0.0285 for this NIR model. The strict NIR calibration region was not found and the large NIR region was used to create the NIR calibration region to predict the 4 of T. Despite the large NIR region the results still are the normal probability distributed and the model is capable to predict the 4 of T.

Accurate NIR model for the 3 of T was not succeeded to create and p-value for this model just was 0.675, and therefore is not statistically significant. The fitted line plot for the NIR model for the 3 of T is presented in the figure 23. The variation of the predicted NIR results cannot be explained by the NIR model and there is no correlation between the reference and NIR results. These facts are provided that the created NIR model is no fitted to the data and then more data need to collect.



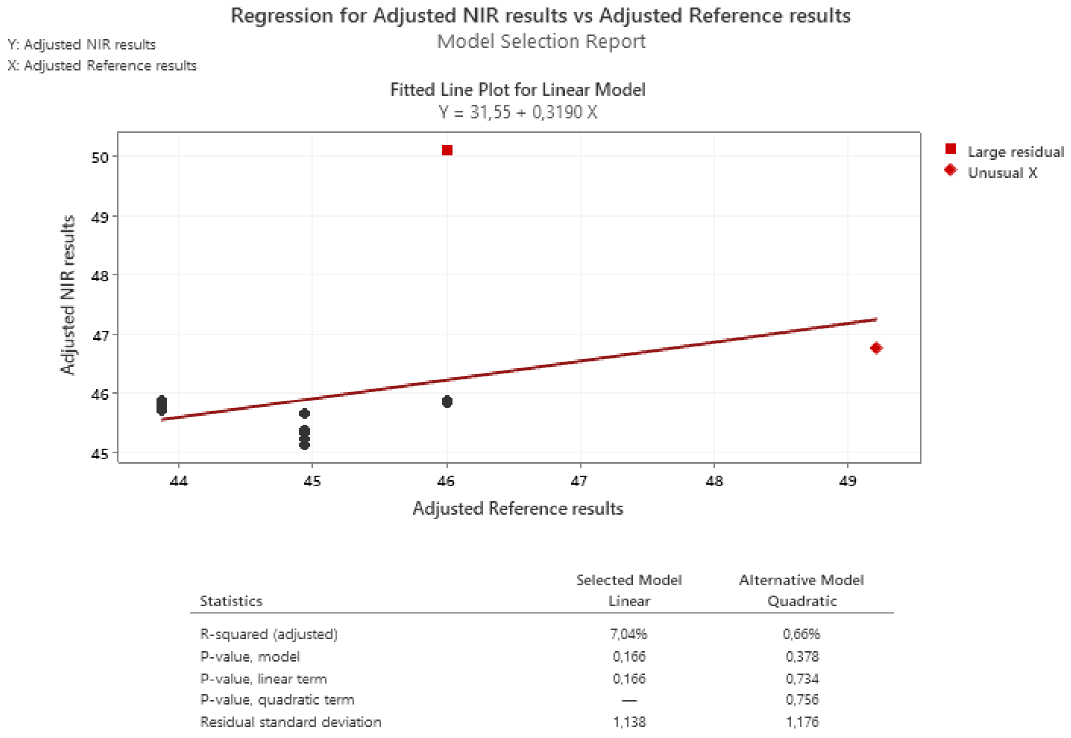
Statistics	Selected Model Linear	Alternative Model Quadratic
R-squared (adjusted)	0,00%	0,00%
P-value, model	0,675	0,920
P-value, linear term	0,675	0,906
P-value, quadratic term	—	0,901
Residual standard deviation	6,839	7,873

Figure 23. Fitted line plot for NIR model to predict 3 of T.

Many sample outliers can be noted from the regression analysis in figure 23 and the outliers are one of the factors to be explained, why the model is not be fitted to the data and the p-value is so high. Alternatively, the reference results shall be variated by the different working-way of the manufacturing operators and further explain the inaccurate NIR model. In fact, the operators were doing the analyses of the 3 in the different manner and therefore was causing the variation for the reference results. Secondly, the NIR measurement based on the vibration of the water molecules and in theory, the NIR is not able to vibrate all water of molecules and therefore the NIR measurement is no reaching the reference results in accurately. However, it’s the sum of many factors to be explained the inaccurate NIR model for the 3 of T.

8.3.2 NIR model for the R

NIR model for the 3 of R was created and the regression analysis for the model is presented in the figure 24. The NIR model is not statistically significant since the p-value for the model is 0.166 and there is enough correlation between the reference and the NIR results. In overall, the sample points follow the NIR model and there are large outliers to impair the NIR model, so without the large outliers the model would be achieved the accuracy model to predict the 3 of R.



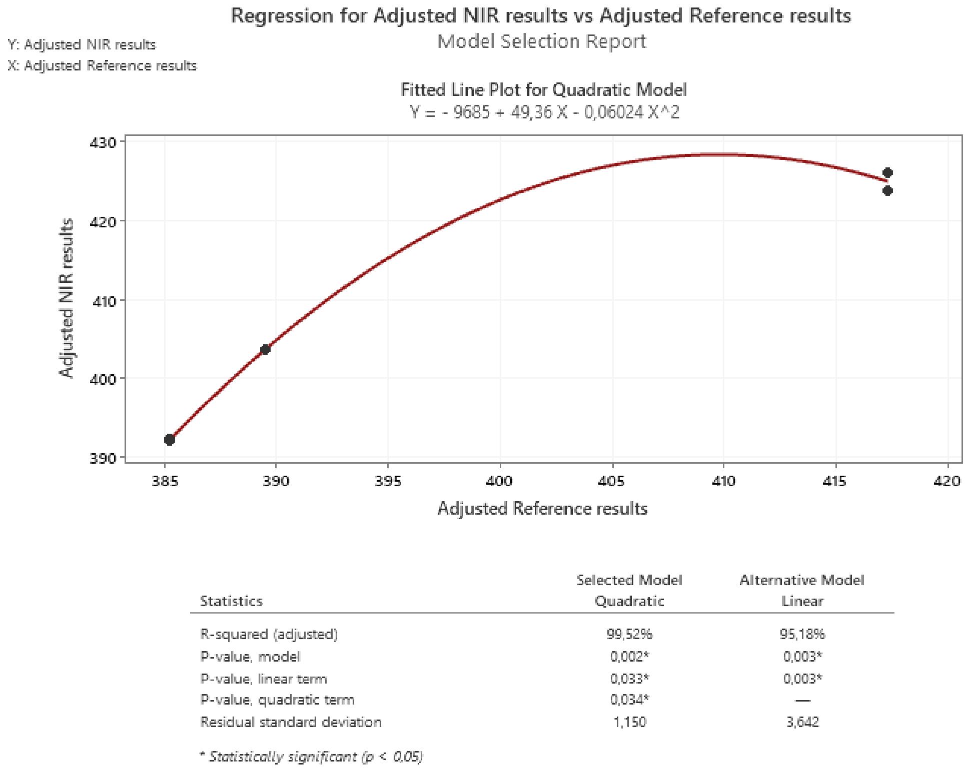
Statistics	Selected Model Linear	Alternative Model Quadratic
R-squared (adjusted)	7,04%	0,66%
P-value, model	0,166	0,378
P-value, linear term	0,166	0,734
P-value, quadratic term	—	0,756
Residual standard deviation	1,138	1,176

Figure 24. Fitted line plot for NIR model to predict 3 of R.

Large outliers can be explained the inaccuracy NIR model or the measurements was not done in the standard condition. Only 13.24 % of variations can be explained with the NIR model and others can be explained with the other factors, such as the variation of the NIR spectra set and the variation of the 3 analysis actions by the manufacturing operators. Furthermore, the NIR model was created using with the NIR region of 4000-12000 cm^{-1} and no strict NIR region was found to measure the 3 using with the NIR technology.

8.3.3 NIR model for the U

NIR model for the 3 of U just was created and the NIR model for the 4 of U has not created since not enough data. The quadratic model to predict the 3 of U is presented in the figure 25 and the results of the model are shown that the quadratic model fits perfectly to the data. In fact, the p-value for this model is 0,002, which is provided that the model is the statistically significant and over 99 % of the variation can be explained by the model.



Statistics	Selected Model Quadratic	Alternative Model Linear
R-squared (adjusted)	99,52%	95,18%
P-value, model	0,002*	0,003*
P-value, linear term	0,033*	0,003*
P-value, quadratic term	0,034*	—
Residual standard deviation	1,150	3,642

** Statistically significant (p < 0,05)*

Figure 25. Fitted line plot for NIR model to predict 3 of U.

Samples size (n = 5) is not large to provide the precise estimation of the strength of the relationship, so more samples need to collect to be 100 % correct to be predicted the 3 for the U. The NIR results are not following the normal probability distribution and there are the large residuals, which are not following the fitted values. This means that the quadratic model is the best correct model to estimate the relationship of the reference and the NIR in the manufacturing.

Large outliers cannot be detected from the regression analysis and the model fits to the data in this case. RMSE for this model is 0.475 and the correlation coefficient achieved 1, so the correlation is very strong.

9 CONCLUSION

Near-infrared (NIR) spectroscopy is according to literature fast, nondestructive and no preparation method needed for the analytical tasks in process industry. In fact, it just takes under 10 seconds to measure the samples, which contain the organic compounds and the concentration of the analyte samples exceeding 0.1 %. Today, the NIR technology is used in many industry fields of the engineering.

The NIR technology has potential to reduce the hazardous samples in the Kitee site, but it is needed many samples to be created the accuracies NIR models to measure the properties of the resin material in Kitee. In fact, the NIR must learn which are the important in the samples and it is the time-consuming to create the calibration models using with the NIR. The NIR models are needed approximately 40-50 samples to be created the NIR models, which are the capable to predict any properties from the resin materials. It is not difficult to procedure, but it needs patience and the good sampling plan to proceed it in the site.

Procedure to be created the NIR models were presented in the subchapter 7.2 and which actions are needed to create the NIR in the manufacturing site. Collecting the calibration samples by the manufacturing operators, analyzing the samples using with the traditional analytical method and setting the NIR spectra for sample are the main actions to proceed NIR models in practical. During the master thesis process 3 potential resin materials (T, R and U) were selected to creating the NIR models since these resin materials had enough data to proceed the NIR models procedure.

According to the literature 1 peak for the NIR region need find, if wanted to measure any substance or concentration. However, just for the resin material of T was found the 1 peak for the NIR region to measure the absorbances. The aqueous concentration of 1 can be measured using with the aromatic compound to be vibrated in the NIR technology and the 2 is measured using with the water molecules, which are vibrating. For others analyzes were not found 1 peak to measure the properties of the samples in Kitee site. These findings are provided that the chemical properties can be measured with the NIR using with 1 peak, whereas the physical properties are not needed this 1 peak in the NIR technology.

Results were provided that more data is needed to evaluate the practical of the NIR in Kitee site, but still was shown the NIR was measuring the same values for the properties as the reference methods in the laboratory. The most potential NIR models were created for the resin materials of T and U. The aqueous concentration of 1 for the T shall be measured with the NIR, if more data will be collected and the proper model will be created with the NIR technology. The outliers should be deleted from the data and fit the model for the data, as required in the NIR.

NIR technology has huge potential to link for the distributed control system (DCS) and it has own constraints, as well. NIR probes can be installed to the side of the reactors or the pipelines and there are possibilities measure various resin materials in Kitee site. However, for each property of the resin material is needed to create the own NIR model to measure the properties using with the NIR and the teaching data is needed to be used during the NIR model procedure. The validation data is used to validate the NIR models and checking that the model structure as best as possible, and the testing data is used to test its utility in the site.

Preventive maintenance for the NIR, the change of the NIR fibers and the cleaning of the NIR sensors are required, if the NIR technology is going to use in the manufacturing site as continuously. In fact, there was noted that the NIR probe was needed to clean in weekly, so that the NIR spectra is as clear as possible to measure the concentrations of the samples. The crud of the resin material made it difficult to create the definite NIR spectra and further made difficult to proceed the accuracies NIR models. The exact preventive maintenance plan is needed to plan, if using the NIR in the manufacturing site and increase the productivity.

NIR is more suitable for the high 3 resin materials, because the clear NIR spectra was received from the higher 3 materials in the Kitee site. The good reason was not found this phenomenon, but it’s one of the constraints for the NIR technology. The most suitable resin materials were U and R, whose 3 levels were over 350 mPas.

During the experimental section was noted few points, which need to be concerned in the future. The precise sampling plan is needed to prepare to be preparing the NIR calibration models and achieve the accuracies NIR models to practical state. Preferred to select the pair potential resin materials, which are produced the most in the manufacturing site and their 3 levels are high for the NIR technology. Further, the manufacturing operators need to coach to analyze the hazardous samples with the NIR and collect data as continuous. It is very important that the data is collecting in the standard condition and each sample is analyzed in the same manner.

NIR is preferred to use in the laboratory conditions in first since the data is obtained and the manufacturing operators are used to use the NIR technology in the manufacturing site. If used the NIR probe in the laboratory, then the NIR probe is needed to clean with the methanol after each analysis action in the laboratory. There was noted that methanol is the best solvent to dissolve any crud or dirt from the NIR probe. Furthermore, the NIR is needed to arrange PC, which is using the OPUS program to collect all NIR spectra and constructing NIR models. This PC should be as newest as possible to be eliminated any stopping or failure for the NIR.

Uniformity of the NIR results and further the accuracy of the NIR models are the most important factors to be implementing the NIR technology to the manufacturing site. To at this point, the calibration samples have collected too little and the calibration models are needed 40-50 samples to be created the accuracies NIR models and fit the NIR models to the data. Therefore, the main research and development targets are to be creating the accuracies NIR models and try to be fit the models to data. The more interesting issues are to find out the differences of the NIR models for the same material and property, if the models have been created in the resin plant.

According to the master thesis results there were not found the 1 peak to measure the properties of 3 and 4 for the resin materials. In the future, it would be interesting to research the possibilities to use some peak region of the NIR and which compounds can be used to measure the properties of 3 and 4. It is very important to be created the accuracies NIR models and the literature is said that 1 peak should be used to measure the concentrations of any substance using with the NIR technology.

Furthermore, the NIR technology is preferred to be tested to the continuous processes, such as for the formalin plant in the Kitee site. In fact, the formalin plant is the most critical plant in the Kitee site and recommended to be investigated the possibilities to use the NIR technology for the formalin plant. The questions are raised how reliably and fast can be measure the concentration of the formaldehyde or methanol and does it need any cleaning action for the NIR probes.

10 SUMMARY

The purpose of this master’s thesis was to study the possibilities to reduce the hazardous samples of the resins and investigate the potential of the NIR for the reduction in the Kitee plant. So far, the main hazardous samples are the phenolic and the aldehydic samples for the employees’ health and the slow analysis process to analyze the 2 of the resin products. In fact, the experimental section focused on investigating the potential of the NIR for the Kitee plant and to be reduced the hazardous samples. The actions and the proposed suggestions also were included to reduce the number of the hazardous samples and optimizing the calibration NIR models for the Kitee plant.

Potential of the NIR was investigated on the literature and the experimental section, which was arranged from August to December in 2020 in the Kitee plant. Data was collected from the batch reactors R-4 and R-5, but the NIR measurements were done in the manufacturing laboratory. The exact sampling plan was prepared for the experimental section and the data was collected as continuously. According to the experimental results there were not the statistically significant data based on the t-test procedure and it can be said that NIR is the suitable technology, if is considered the reference results to the NIR results. The measured results of the means and the standard deviations were similar compared to the reference results, but there were few outliers within the data.

NIR has still some constraints, such as the unexpected stopping or failure for the NIR matrix or the fibers. The PC of the NIR is needed to start again and again, which made difficult to collect the teaching data for the calibration NIR models. The NIR probes were needed to clean at weekly, so that the NIR spectra would be as clear as possible and methanol is preferred to be used to cleaning. In fact, the NIR technology is very sensitive for all failures, therefore it needs the preventive maintenance in the Kitee plant.

The NIR models were not so accuracies as expected, but the NIR technology is required more data to be creating the accuracies models, which p-value is under 0.05 and therefore are the statistically significant to be used in the manufacturing. In fact, approximately 40-50 samples are needed to be creating the accuracies NIR models, which are capable to predict the real values and further to reduce the hazardous samples in the Kitee plant.

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Appendix 1

Group frequencies in the Near-Infrared Region

1) Methyl -CH_3

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Combination	2275-2285	4400-4380	CH stret. + CH bend.
	1355-1365	7380-7330	
	1010-1020	9900-9800	
First overtone	1710-1730	5850-5780	first overtone of asym.stret
	1770-1785	5650-5600	first overtone of sym.stret
Second overtone	1150-1165	8700-8580	second overtone of asym.stret
	1190-1200	8400-8330	second overtone of sym.stret
Third overtone	870-885	11490-11300	third overtone of asym.stret
	900-910	11110-10990	third overtone of sym.stret

2) Methylene -CH_2

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Combination	2320-2330	4310-4290	CH stret. + CH bend.
	2305-2315	4340-4320	
	1410-1420	7090-7040	2xCH stret. + CH bend.
	1390-1400	7190-7140	
	1050-1060	9520-9430	
First overtone	1735-1750	5760-5710	first overtone of antisym.stret.
	1780-1795	5620-5570	first overtone of sym.stret.
Second overtone	1170-1180	8550-8470	second overtone of antisym.stret.
		8330-8260	
	1200-1210		second overtone of sym.stret.
Third overtone	885-895	11300-11170	third overtone of antisym.stret.
	910-920	10990-10870	third overtone of sym.stret.

3) -CH

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
First overtone	1755-1775	5700-5630	
Second overtone	1185-1195	8440-8370	
Third overtone	900-910	11110-10990	

4) alkenes (vinyl, vinylidine, vinylene)

Overtone	**Wavelength / nm**	**Wavenumber / cm^{-1}**	**Remarks**
Combination	2340-2350	4270-4260	CH_2 stret. +=CH_2 bend.
	2185-2195	4580-4560	CH_2 stret.+C=C stret.
	2135-2143	4680-4660	=CH stret.+C=C stret.
First overtone	1675-1695	5970-5900	
	1645-1660	6080-6020	Vinyl group
Second overtone	1130-1145	8850-8730	
	1110-1120	9010-8930	Vinyl group
Third overtone	860-870	11630-11490	
	840-850	11900-11760	Vinyl group

5) -C=CH alkynes

Overtone	**Wavelength / nm**	**Wavenumber / cm^{-1}**	**Remarks**
First overtone	1535-1545	6510-6470	
Second overtone	1035-1045	9660-9570	
third overtone	780-790	12820-12660	

6) CH (aromatic)

Overtone	**Wavelength / nm**	**Wavenumber / cm^{-1}**	**Remarks**
Combination	1440-1450	6940-6900	2xCH stret.+CH bend.
	1410-1420	7090-7040	2xCH stret.+CH bend.
	1070-1085	9350-9220	2xCH stret.+2xC-C stret.
First overtone	1680-1690	5950-5920	
Second overtone	1130-1140	8850-8770	
Third overtone	850-860	11760-11630	

7) H_2O

Overtone	**Wavelength / nm**	**Wavenumber / cm^{-1}**	**Remarks**
Combination	1930-1940	5180-5120	OH stret.+OH bend.
	1375-1385	7270-7220	OH anti-sym. stret.+OH sym. stret.
First overtone	1450-1460	6900-6850	
Second overtone	975-985	10260-10150	
Third overtone	740-750	13510-13330	

8) free -OH alcohol

Overtone	**Wavelength / nm**	**Wavenumber / cm^{-1}**	**Remarks**
Combination	2060-2090	4850-2060	OH stret.+OH bend.
first overtone	1395-1425	7170-7020	
Second overtone	2370-2390	4220-4180	second overtone of OH bend.
	940-955	10640-10470	second overtone of OH stret.
Third overtone	730-745	13700-13420	

9) OH alcohol

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
First overtone	1435-1480	6970-6760	intermolecular hydrogen bond
	1500-1595	6670-6270	intermolecular hydrogen bond
Second overtone	980-990	10200-10100	intermolecular hydrogen bond
	1035-1045	9660-9570	intermolecular hydrogen bond

10) COOH carboxylic acids, COOR esters

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Second overtone	1890-1920	6290-5210	2xC=O stret. (carboxylic acids)
	1930-1950	5180-5130	2xC=O stret. (esters)

11) C=O ketones

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Second overtone	1950	5130	

12) CHO aldehydes

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Combination	2190-2210	4570-4520	CH stret.+C=O stret.

13) Epoxides

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
First overtone	1640-1650	6100-6060	first overtone of CH stret.

14) -NH_2 primary amines

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Combination	1970-2010	5080-4980	NH stret.+NH bend.
First overtone	1520-1540	6580-6490	first overtone of NH_2 sym.stret
	1500-1520	6670-6580	first overtone of NH_2 antisym.stret.
	1450-1480	6900-6760	$ArNH_2$
Second overtone	1020-1040	9800-9620	second overtone of NH_2 sym.stret
	1000-1020	10000-9800	second overtone of NH_2 anti-sym.stret.
	980-1020	10200-9800	$ArNH_2$
Third overtone	800-820	12500-12200	third overtone of NH_2
	780-800	12820-12500	$ArNH_2$
	770-790	12990-12660	third overtone of NH_2 antisym.stret.

15) -NH$_2$ secondary amines

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
First overtone	1490-1545	6710-6470	
Second overtone	1010-1040	9900-9620	

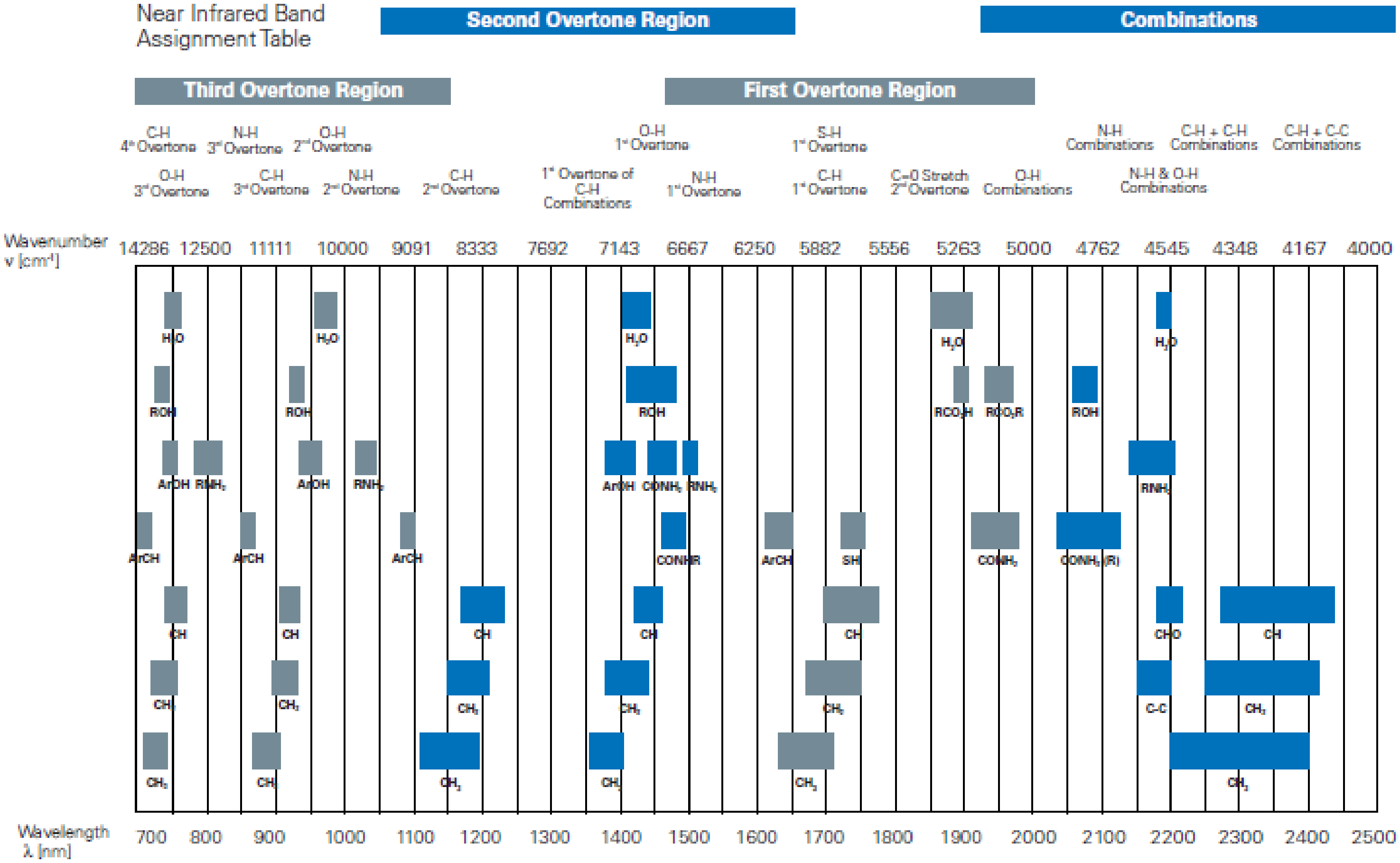
16) -CONH$_2$ primary amides

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Combination	2140-2170	4670-4610	2xamide+amide
	2100-2130	4760-4690	NH stret.+amide
	2040-2060	4900-4850	NH stret.+amide
	1950-1970	5130-5080	NH stret.+amide
First overtone	1600-1620	6250-6170	intermolecular hydrogen bond
	1510-1530	6620-6540	intermolecular hydrogen bond
	1490-1510	6710-6620	first overtone of NH$_2$ sym.stret.
	1440-1460	6940-6850	first overtone of NH$_2$ antisym.stret.
Second overtone	2020-2040	4950-4900	second overtone of amide
	1070-1090	9350-9170	intramolecular hydrogen bond
	1015-1035	9850-9660	intramolecular hydrogen bond
	1000-1020	10000-9800	second overtone of NH$_2$ sym.stret.
	970-990	10310-10100	second overtone of NH$_2$ anti-sym.stret.

17) -CONH- secondary amides

Overtone	Wavelength / nm	Wavenumber / cm^{-1}	Remarks
Combination	2150-2170	4650-4610	2xamide+amide
	2100-2120	4760-4720	NH stret.+amide
	1990-2010	5030-4980	NH stret.+amide
First overtone	1530-1670	6540-5990	hydrogen bond
	1460-1510	6850-6620	free
Second overtone	1910-1930	5240-5180	second overtone of amide
	1035-1120	9660-8930	hydrogen bond
	1000-1050	10000-9520	free

Illustrative diagram of the overtone regions and the combination band region



Appendix 3

List of near infrared spectroscopy results during the experimental section in Kitee plant in 2020

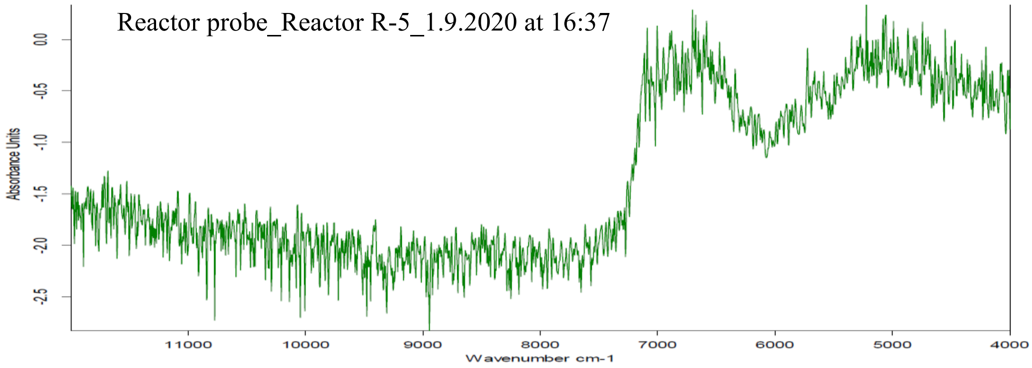
Material	Date	Time	Batch Reactor	Recipe stage	Batch number	Volume of sample (ml)	Temperature (°C)	Time for NIR	NIR probe	Analysis	Reference result	NIR result	Residual
T	1.9.2020	16:42	R-5	Final	KF0JR5000	500	25	16:37	Reactor	1	0,25	0,24	0,0063
T	3.9.2020	16:25	R-5	Final	KF0JR5003	500	26	16:20	Lab	1	0,22	0,24	0,0195
T	17.9.2020	13:05	R-5	Final	KF0JR5032	500	40	13:05	Lab	1	0,21	0,22	0,0101
T	28.10.2020	11:12	R-5	Final	KF0KR5069	900	34,6	11:26	Lab	1	0,21	0,20	0,0053
T	29.10.2020	20:30	R-5	Final	KF0KR5073	700	25	20:32	Lab	1	0,26	0,24	0,0232
T	8.12.2020	14:35	R-5	Final	KF0MR5013	500	20	14:41	Lab	1	0,23	0,24	0,0052
T	1.9.2020	16:42	R-5	Final	KF0JR5000	500	25	16:37	Reactor	2	46,2	46,13	0,07
T	3.9.2020	16:25	R-5	Final	KF0JR5003	500	26	16:20	Lab	2	46	46,21	0,21
T	17.9.2020	13:05	R-5	Final	KF0JR5032	500	40	13:05	Lab	2	46,4	46,2	0,2
T	28.10.2020	11:12	R-5	Final	KF0KR5069	900	34,6	11:26	Lab	2	46,10	46,33	0,23
T	29.10.2020	20:30	R-5	Final	KF0KR5073	700	25	20:32	Lab	2	46,2	46,31	0,11
T	8.12.2020	14:35	R-5	Final	KF0MR5013	500	20	14:41	Lab	2	46,4	46,23	0,17
T	1.9.2020	16:42	R-5	Final	KF0JR5000	500	25	16:37	Reactor	4	1,74	1,72	0,019
T	3.9.2020	16:25	R-5	Final	KF0JR5003	500	26	16:20	Lab	4	1,7	1,728	0,028
T	17.9.2020	13:05	R-5	Final	KF0JR5032	500	40	13:05	Lab	4	1,70	1,683	0,017
T	28.10.2020	11:12	R-5	Final	KF0KR5069	900	34,6	11:26	Lab	4	1,73	1,787	0,057
T	29.10.2020	20:30	R-5	Final	KF0KR5073	700	25	20:32	Lab	4	1,78	1,757	0,023
T	8.12.2020	14:35	R-5	Final	KF0MR5013	500	20	14:41	Lab	4	1,82	1,77	0,046
T	1.9.2020	16:42	R-5	Final	KF0JR5000	500	25	16:37	Reactor	3	94	89,01	4,99
T	3.9.2020	16:25	R-5	Final	KF0JR5003	500	26	16:20	Lab	3	92	89,91	2,09
T	17.9.2020	13:05	R-5	Final	KF0JR5032	500	40	13:05	Lab	3	92	93,64	1,64
T	28.10.2020	11:12	R-5	Final	KF0KR5069	900	34,6	11:26	Lab	3	83	88,12	5,12
T	29.10.2020	20:30	R-5	Final	KF0KR5073	700	25	20:32	Lab	3	78	90,17	12,17
T	8.12.2020	14:35	R-5	Final	KF0MR5013	500	20	14:41	Lab	3	93	76,85	16,15

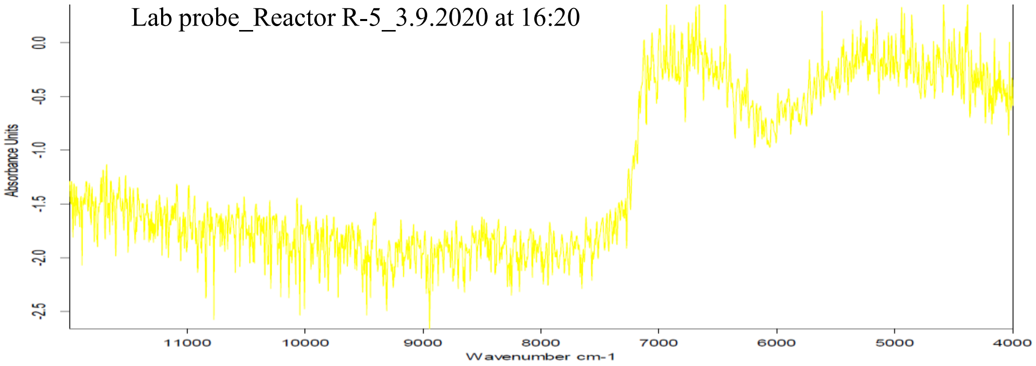
Appendix 3

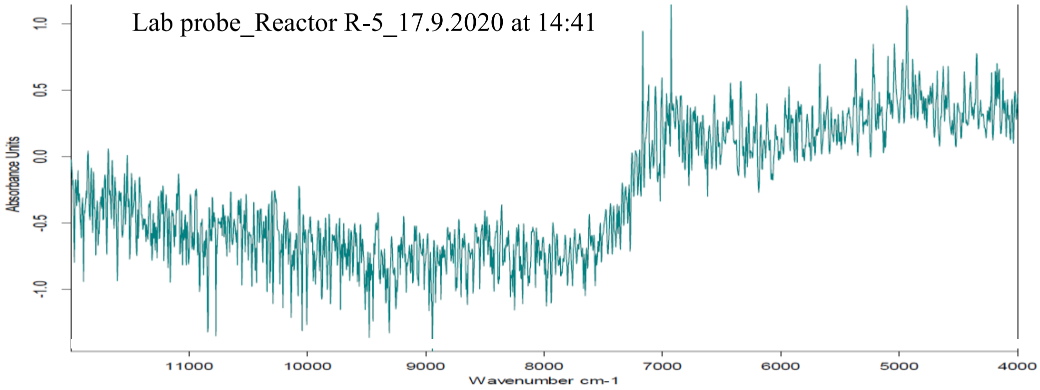
R	27.8.2020	18:25	R-4	Final	KF0HR5043	500	20	18:20	Reactor	3	42	41,88	0,12
R	18.9.2020	3:47	R-5	Final	KF0JR5039	500	22	3:47	Lab	3	46	42,91	3,09
R	21.9.2020	3:45	R-5	Final	KF0JR5041	500	19,6	3:45	Lab	3	43	45,97	2,97
R	29.10.2020	8:18	R-4	Final	KF0KR4056	900	25	8:19	Lab	3	42	41,40	0,6
R	29.10.2020	8:18	R-4	Final	KF0KR4056	900	25	8:20	Lab	3	42	41,49	0,51
R	29.10.2020	8:18	R-4	Final	KF0KR4056	900	25	8:21	Lab	3	42	41,58	0,42
R	29.10.2020	8:18	R-4	Final	KF0KR4056	900	25	8:22	Lab	3	42	41,60	0,4
R	29.10.2020	8:18	R-4	Final	KF0KR4056	900	25	8:23	Lab	3	42	41,62	0,38
R	29.10.2020	8:18	R-4	Final	KF0KR4056	900	25	8:24	Lab	3	42	41,60	0,4
R	2.11.2020	10:50	R-5	Final	KF0LR5012	500	25	11:02	Lab	3	43	42,08	0,92
R	20.11.2020	2:38	R-5	Final	KF0LR5044	500	20	2:46	Lab	3	41	41,99	0,99
R	20.11.2020	2:38	R-5	Final	KF0LR5044	500	20	2:47	Lab	3	41	42,09	1,09
R	20.11.2020	2:38	R-5	Final	KF0LR5044	500	20	2:48	Lab	3	41	42,03	1,03
R	20.11.2020	2:38	R-5	Final	KF0LR5044	500	20	2:49	Lab	3	41	41,99	0,99
R	20.11.2020	2:38	R-5	Final	KF0LR5044	500	20	2:50	Lab	3	41	41,92	0,92
R	26.11.2020	9:00	R-5	Final	KF0LR5064	500	20	9:09	Lab	3	43	42,04	0,96
U	9.9.2020	1:15	R-5	Final	KF0JR5019	500	40	1:10	Lab	4	7,38	7,248	0,132
U	20.9.2020	15:39	R-5	Final	KF0JR5038	500	29,9	15:39	Lab	4	7,23	7,346	0,116
U	30.9.2020	19:18	R-5	Final	KF0JR5062	500	39,8	19:18	Lab	4	7,30	7,299	0,001
U	5.10.2020	19:52	R-5	Final	KF0KR5010	500	25	19:57	Lab	4	7,22	7,25	0,027
U	5.10.2020	19:52	R-5	Final	KF0KR5010	500	25	19:58	Lab	4	7,22	7,25	0,031
U	9.9.2020	1:15	R-5	Final	KF0JR5019	500	40	1:10	Lab	3	364	370,30	6,3
U	20.9.2020	15:39	R-5	Final	KF0JR5038	500	29,9	15:39	Lab	3	360	359,60	0,4
U	30.9.2020	19:18	R-5	Final	KF0JR5062	500	39,8	19:18	Lab	3	360	359,80	0,2
U	5.10.2020	19:52	R-5	Final	KF0KR5010	500	25	19:57	Lab	3	390	390,90	0,9
U	5.10.2020	19:52	R-5	Final	KF0KR5010	500	25	19:58	Lab	3	390	388,80	1,2

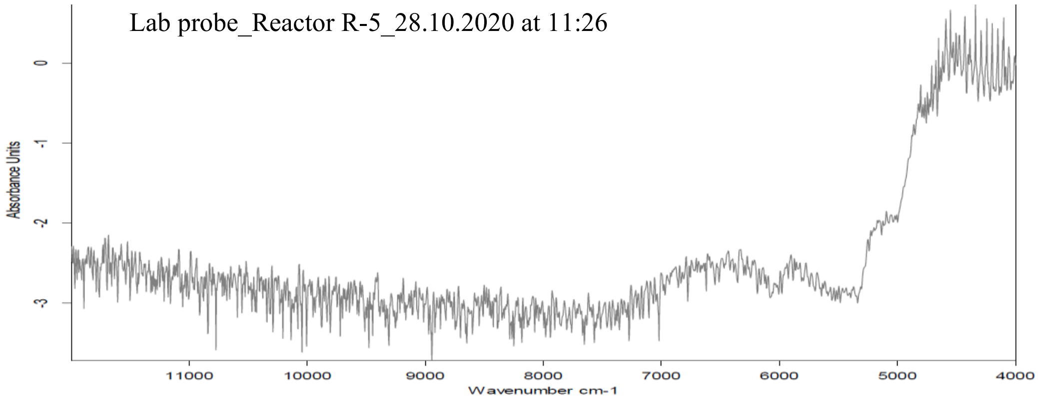
Appendix 4

List of the NIR spectra set for the resin material of T


Reactor probe_Reactor R-5_1.9.2020 at 16:37


Lab probe_Reactor R-5_3.9.2020 at 16:20

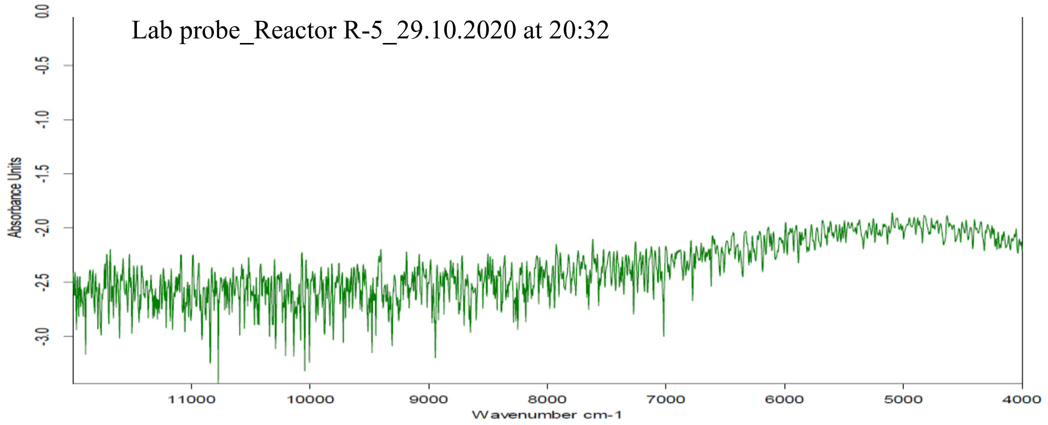

Lab probe_Reactor R-5_17.9.2020 at 14:41


Lab probe_Reactor R-5_28.10.2020 at 11:26

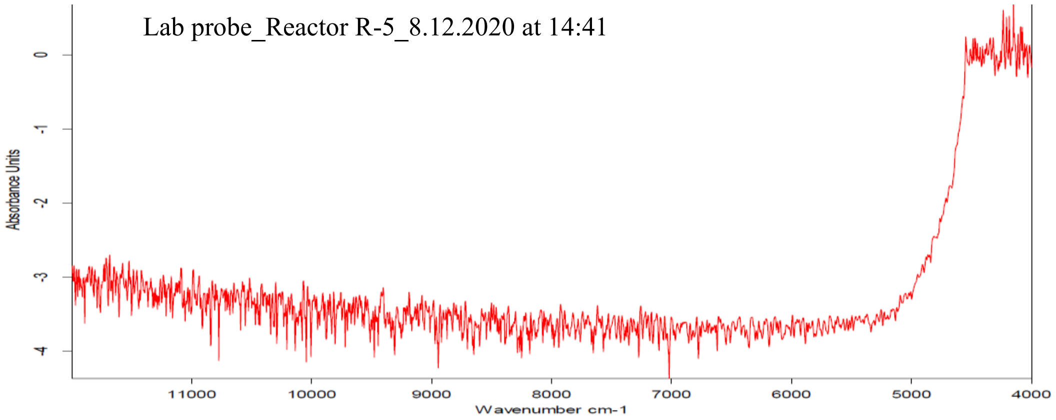
To be continued

Appendix 4

List the NIR spectra for the resin material of T



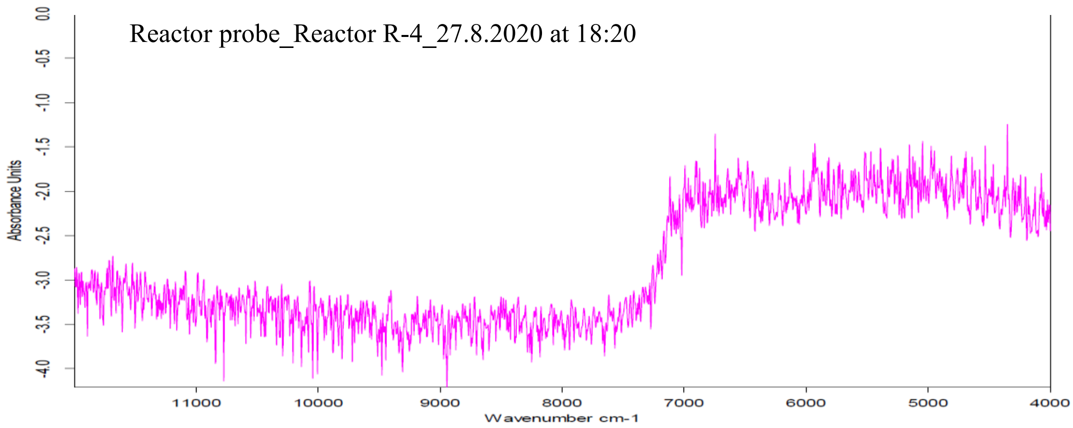
Lab probe_Reactor R-5_29.10.2020 at 20:32

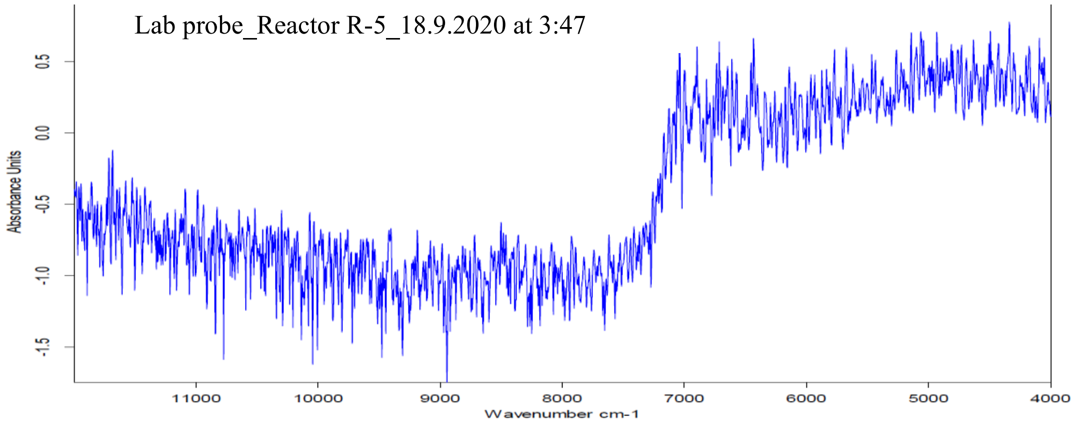


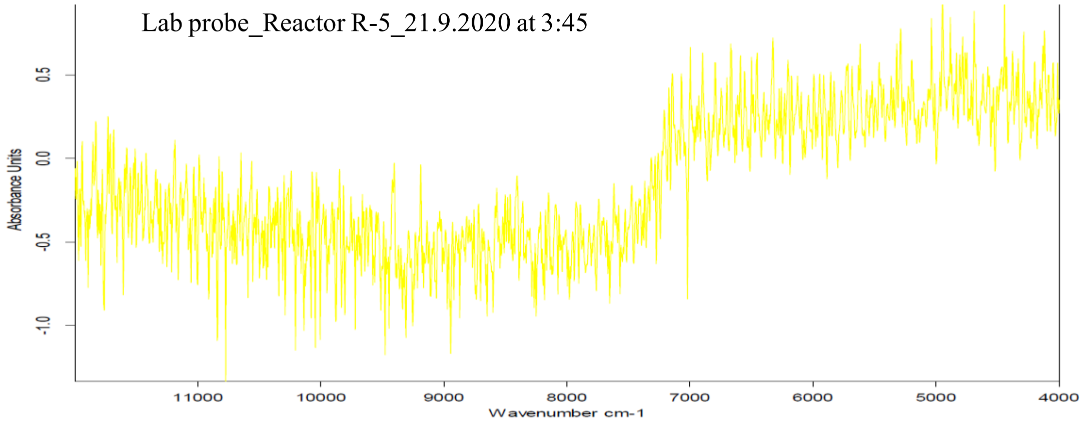
Lab probe_Reactor R-5_8.12.2020 at 14:41

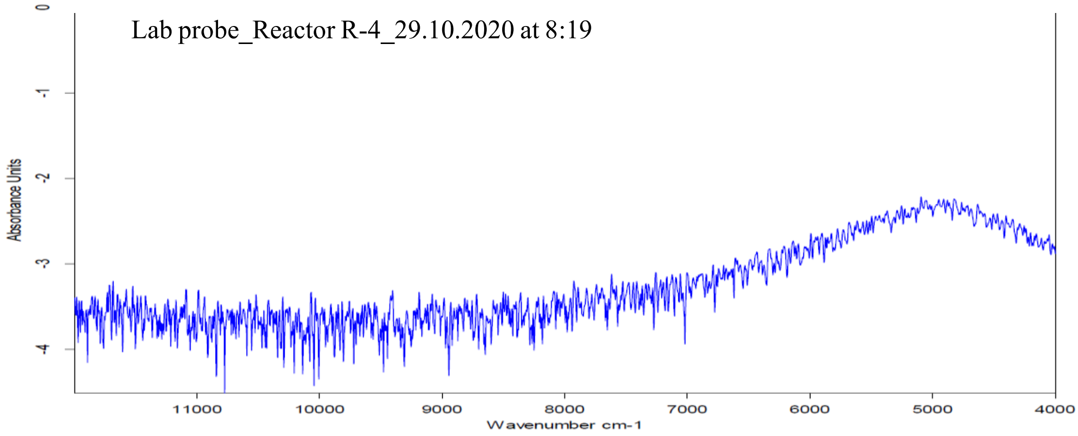
Appendix 4

List the NIR spectra set for the resin material of R


Reactor probe_Reactor R-4_27.8.2020 at 18:20


Lab probe_Reactor R-5_18.9.2020 at 3:47

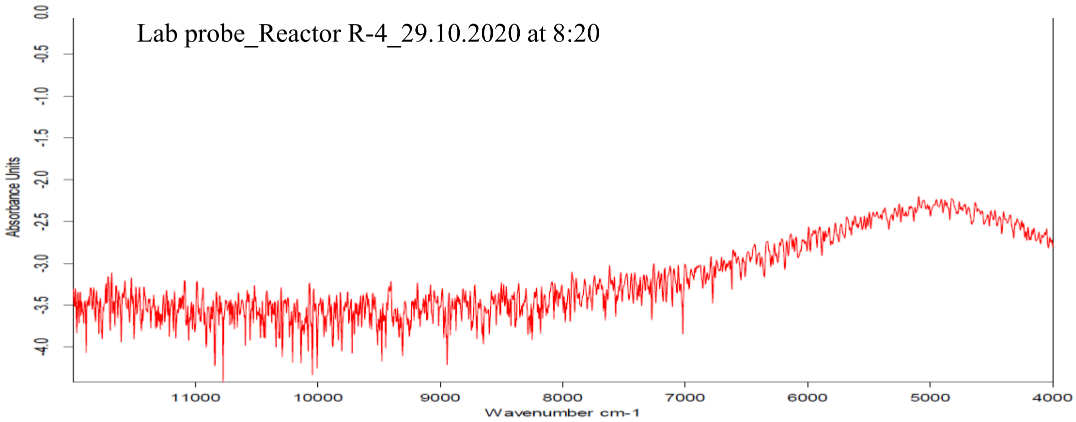

Lab probe_Reactor R-5_21.9.2020 at 3:45

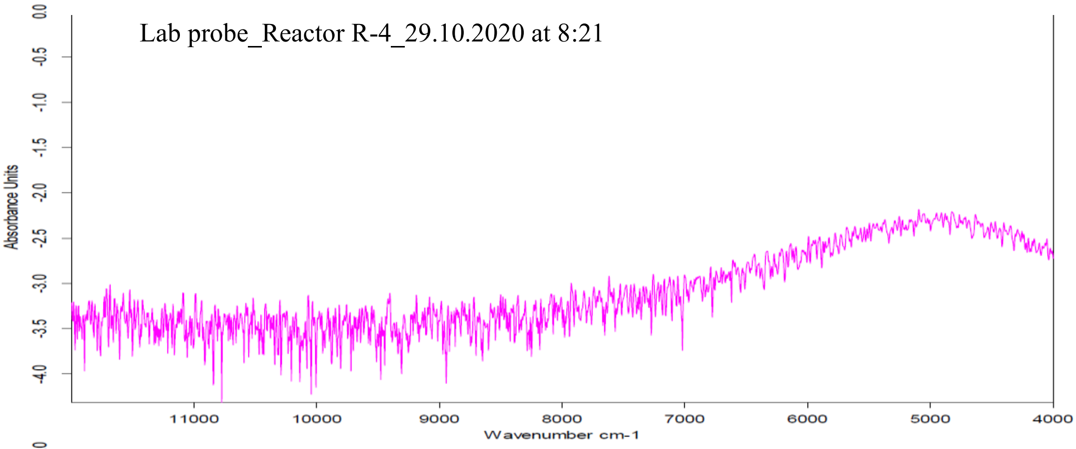

Lab probe_Reactor R-4_29.10.2020 at 8:19

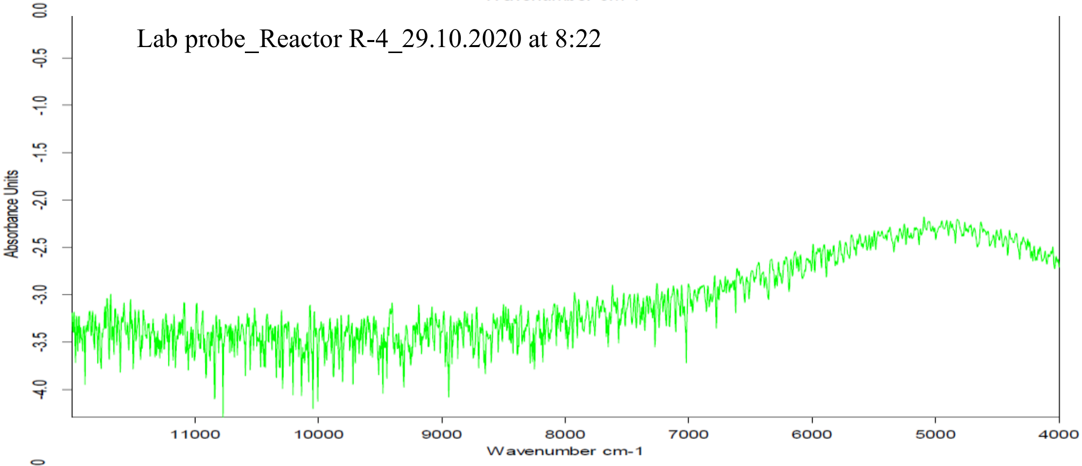
To be continued

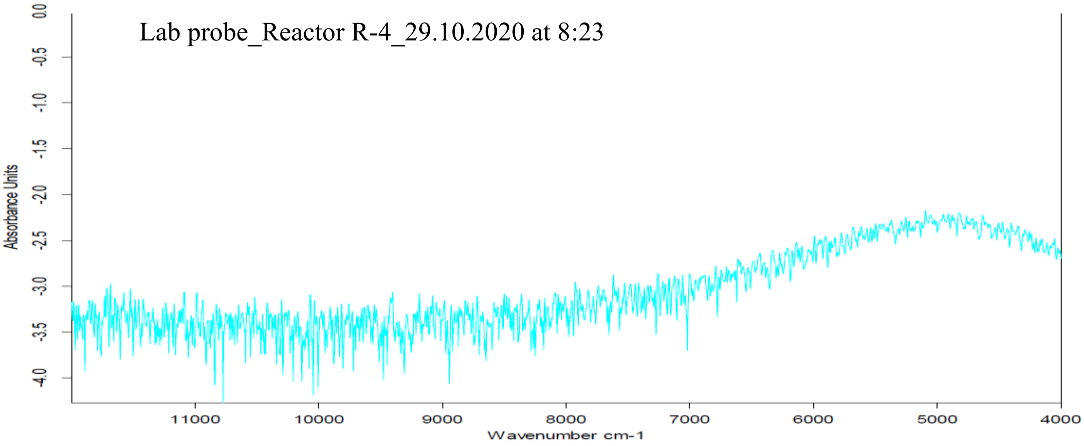
Appendix 4

List the NIR spectra for the resin material of R



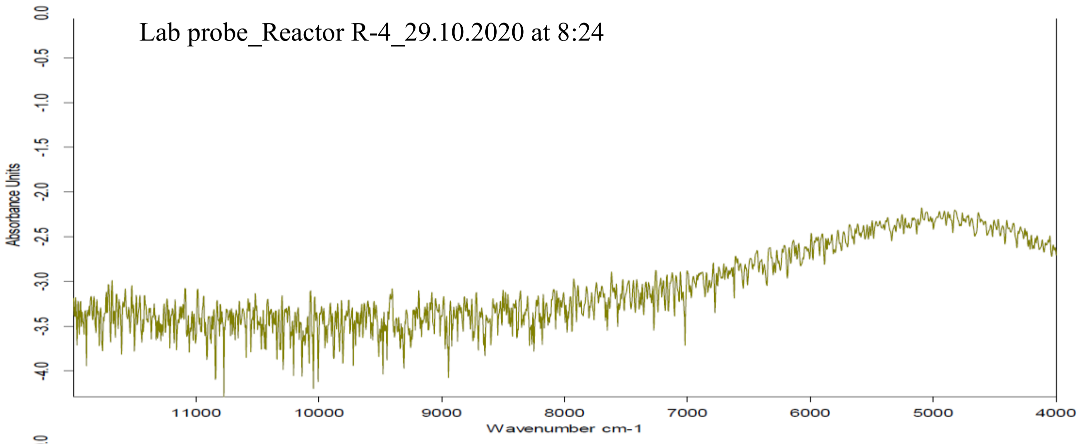




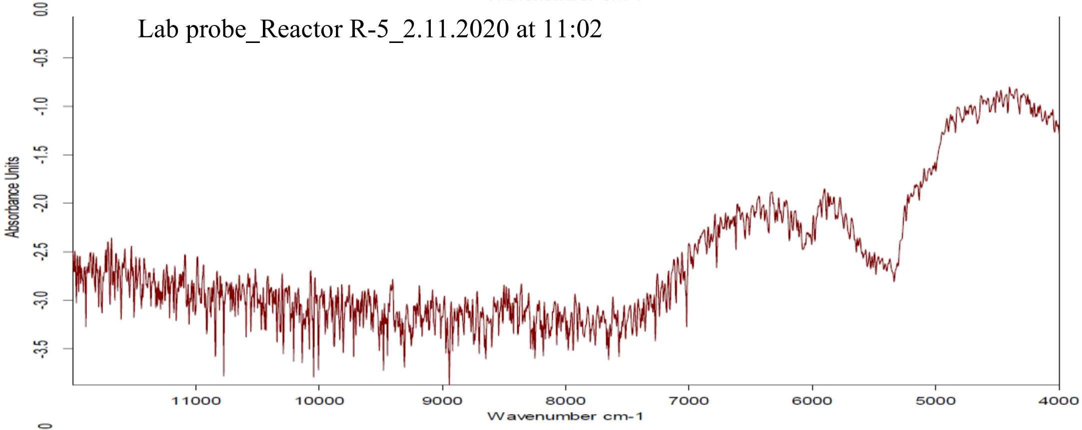


To be continued

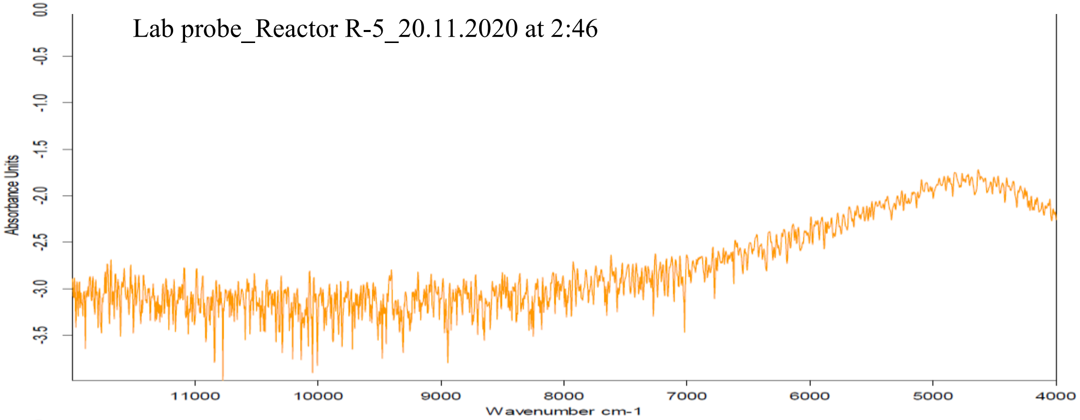
List the NIR spectra for the resin material of R



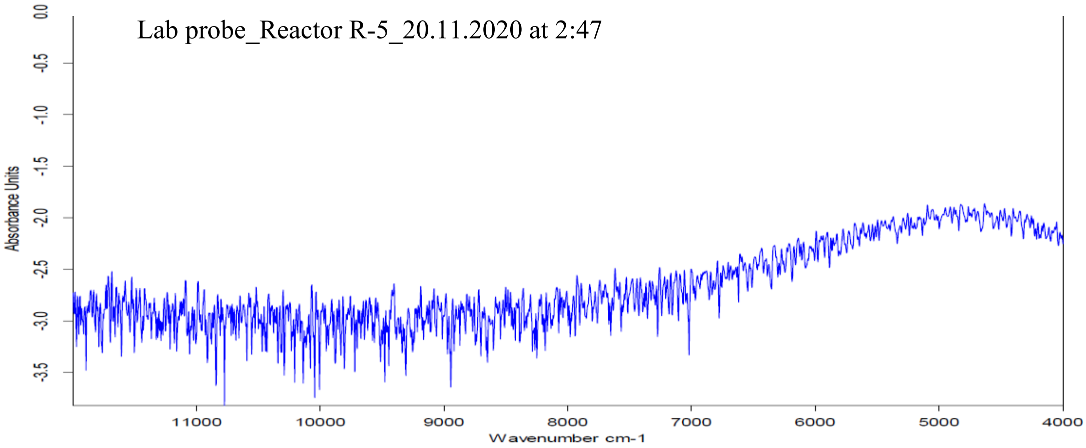
Lab probe_Reactor R-4_29.10.2020 at 8:24



Lab probe_Reactor R-5_2.11.2020 at 11:02



Lab probe_Reactor R-5_20.11.2020 at 2:46

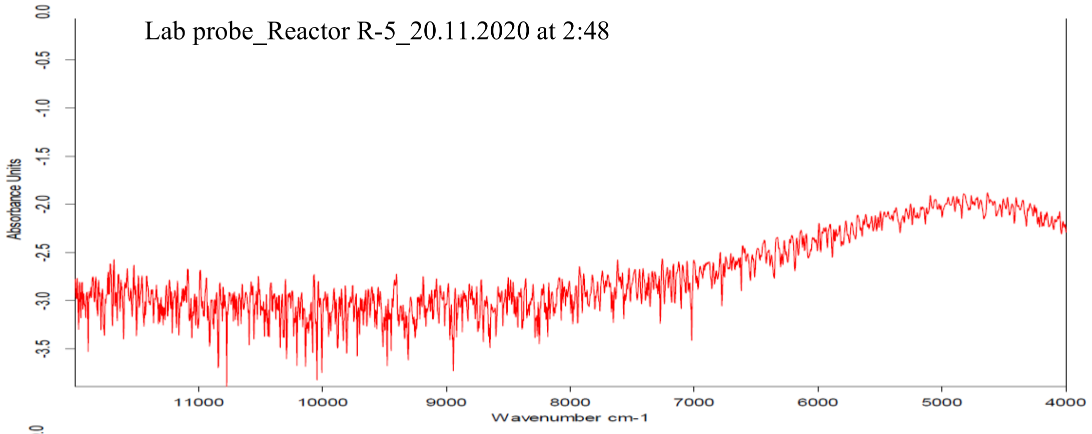


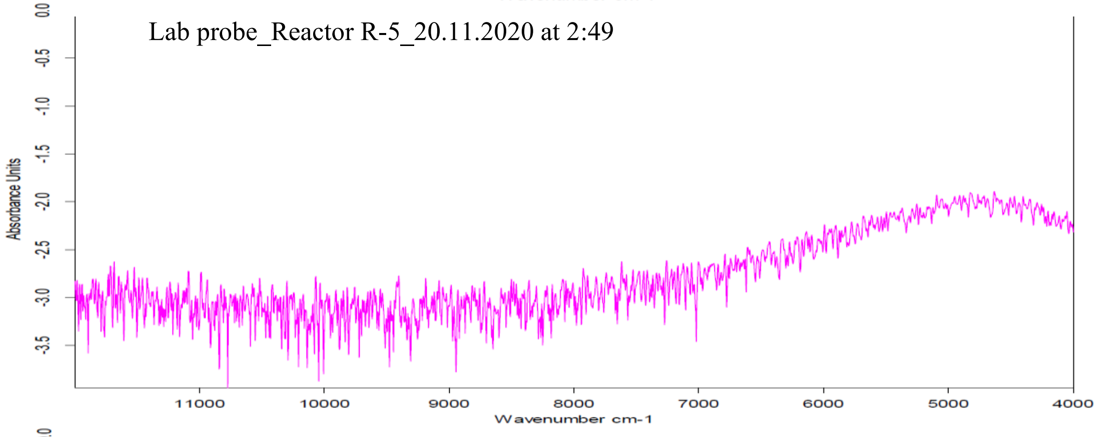
Lab probe_Reactor R-5_20.11.2020 at 2:47

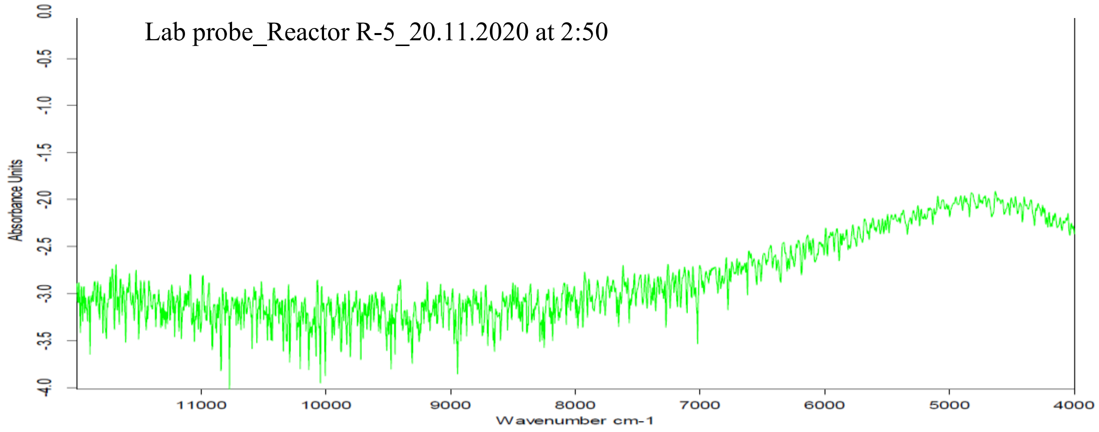
To be continued

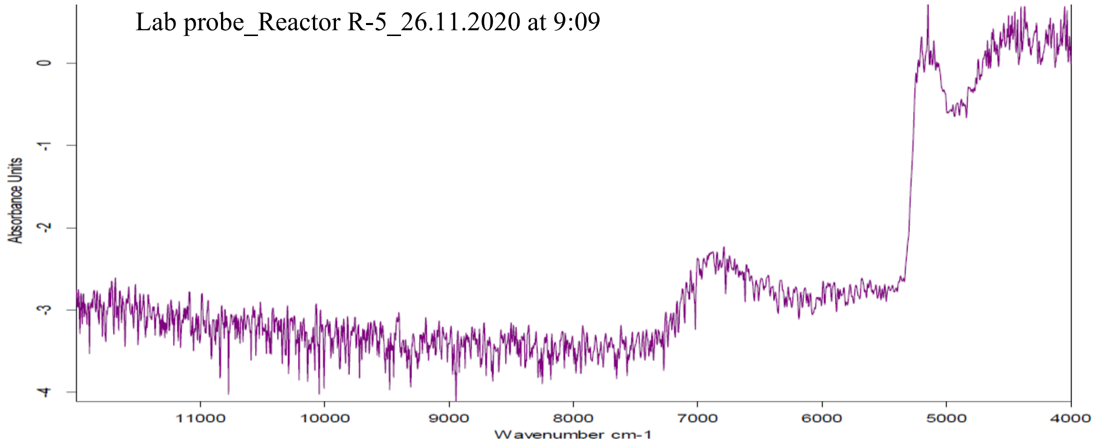
Appendix 4

List the NIR spectra for the resin material of R


Lab probe_Reactor R-5_20.11.2020 at 2:48

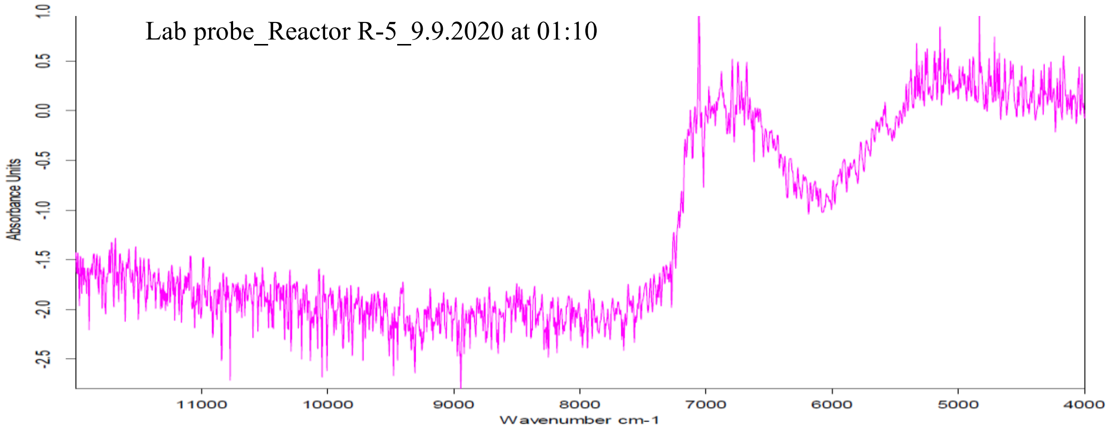

Lab probe_Reactor R-5_20.11.2020 at 2:49

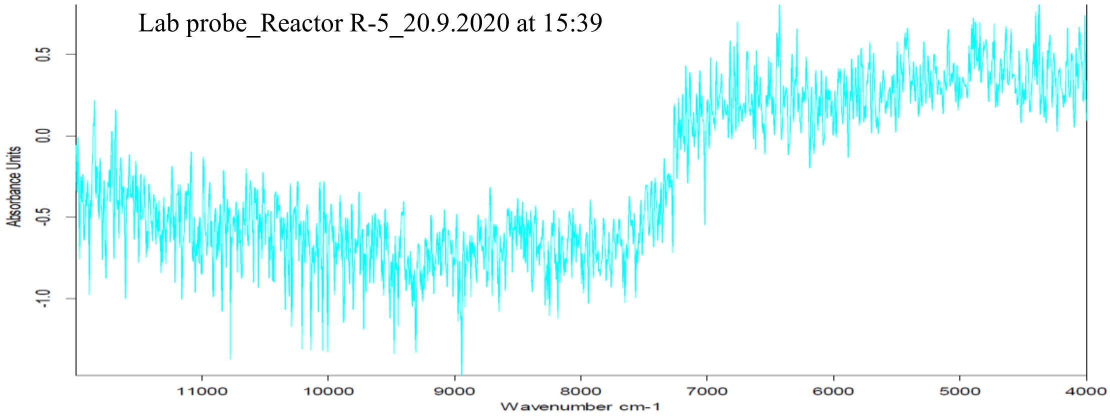

Lab probe_Reactor R-5_20.11.2020 at 2:50

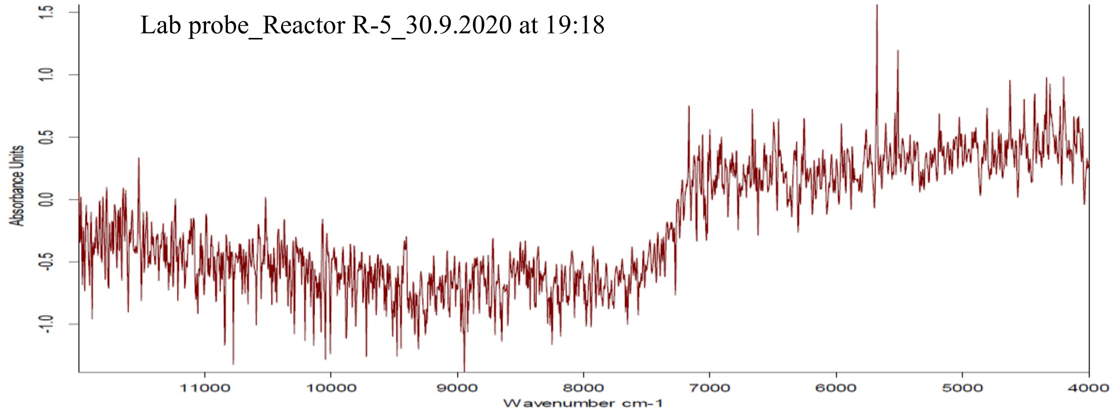

Lab probe_Reactor R-5_26.11.2020 at 9:09

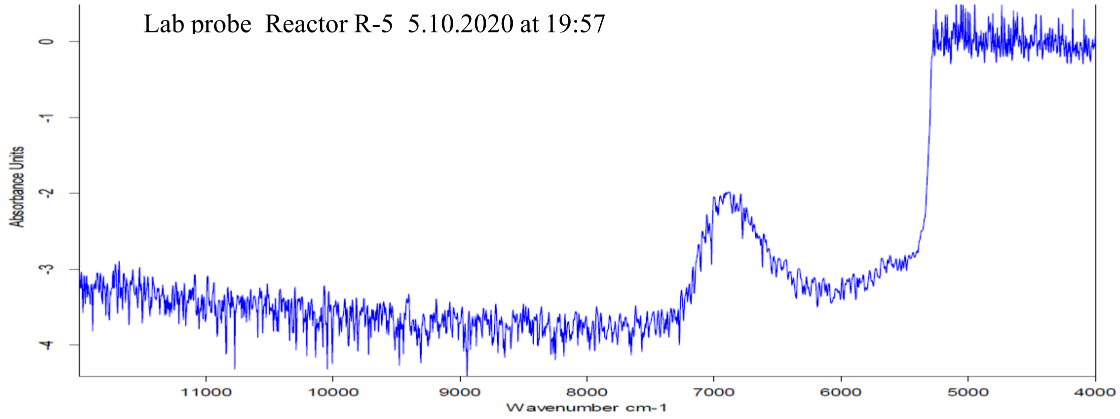
Appendix 4

List the NIR spectra for the resin material of U









To be continued

Appendix 4

List the NIR spectra for the resin material of U